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This report summarizes work done during the first year of a program entitled "Research on Mercury Cadmium Telluride". Progress on the proposed tasks is described, together with a review of accomplishments. These include the design of a new epitaxial reactor, the growth of high quality CdTe and HgCdTe on both GaAs and CdTe substrates, and the development of a comprehensive theory for the growth of CdTe in OMCVD systems.

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ABSTRACT

This report summarizes work done during the first year of a program entitled, "Research on Mercury Cadmium Telluride". Progress on the proposed tasks is outlined here, together with a review of our accomplishments. These tasks include the design of a new epitaxial reactor, the growth of high quality CdTe and HgCdTe on both GaAs and CdTe substrates, and the development of a comprehensive theory for the growth of CdTe in OMCVD systems.

A number of papers have been submitted on our work. These are attached as Appendices to this report.

CONTRIBUTORS

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INTRODUCTION

The goal of this program is to conduct research on Mercury Cadmium Telluride and related compounds. Its emphasis is on the growth and characterization of thin films of these materials by means of Organometallic Vapor Phase Epitaxy. This report outlines tasks proposed and the accomplishments during the first year.

WORK ACCOMPLISHED DURING THE FIRST YEAR

Reactor Upgrade:

An existing epitaxial reactor was adapted to meet the special research needs of this program, during the early months of our effort. Specifically, one mass flow controller channel was installed for the cadmium source, and a new graphite susceptor was designed and incorporated into the reactor. In addition, many of the lines were removed and replaced with new plumbing. Since that time, a total of 250 runs of CdTe and MCT have been made on this system.

A new reaction chamber, with a simplified loading system, has also been designed and fabricated. This has not as yet been installed on the system, because of the down time entailed by this process.

A new reactor, capable of large area slices, was designed and components ordered for it. Construction of this system is well in hand, and is about 10 months ahead of schedule. At the present time, we are held up on its completion by delays in the delivery of the quartz reaction chamber and the reactor loading system This system is an all welded unit, with VCR fittings and mass flow controllers on all its channels. Operation at pressures from 1 atm to 0.1 atm will be possible under closed loop control. Both manual and full computer control have been incorporated into this

machine. The initial software for running this system has been written; however, additional refinements will be made once the system is operational.

Work was initiated on the growth of MCT on InSb substrates as well as on a GaAs substrates. Our early results showed that the use of InSb would result in massive doping by out-diffusion from the substrate, so the effort was shifted to the growth of MCT on GaAs. Here, we first grew CdTe on GaAs, and established that it was of sufficient quality to growth subsequent high quality epitaxial layers of MCT. Layers of this type were grown for a series of CdTe buffer layer thicknesses and MCT compositions. Our findings are that:

a) For all compositions, the layers were n-type. The mobility of these layers increased with increasing buffer layers thickness, but reached a limit for CdTe layer thicknesses in excess of 2.5 microns.

b) Experiments on CdTe layers grown at 350°C and heat treated to simulate the subsequent growth of MCT (415°C for 75 min) have shown very little out diffusion of gallium into the CdTe. These experiments have involved measurements of the breakdown voltage of p-n diode4s on the CdTe layer, and SIMS profiling. We conclude that the n-type behavior is primarily due to defects in MCT layers grown with their buffers, and not from gallium out diffusion.

c) A mobility of 250,000 cm^2/V-sec was obtained at 77K in a number of layers with x = 0.2, for CdTe buffer layers of 2.5 microns. Buffer layers, 1000 $\mathring{A}$ thick, resulted in mobilities around 10,000 cm^2/Vsec. The direct growth of MCT on GaAs was also tried. However, this was discontinued after a few runs, because of the poor layer quality resulting from this approach.

d)   A composition accuracy of ± 5% was obtained over samples 1.5 cm × 1.5 cm in size. This is certainly a problem area, because of the small reaction chamber (50 min ID) in which layer growth is carried out. Work with larger samples is planned once the new reactor comes on stream.

A detailed study has been made to determine the reaction mechanisms for the growth of CdTe. This study involved growth on a variety of substrates (CdTe, InSb, GaAs and Al_2O_3) in addition to an extensive study of the results of other workers. In this work, we have shown that it is possible to grow CdTe from elemental cadmium and DETe, at temperatures as low as $230^{\circ}C$. Thus, there is no a priori reason to postulate the formation of a DMCd-DETe adduct to accomplish this low temperature growth. In addition, our experiments indicate that CdTe growth begins by the hterogeneous decomposition of DMCd to cadmium, which is chemisorbed on the surface. This process is the rate limiter in the growth of CdTe, and also in the growth of other cadmium compounds (CdS, CdSe) from alkyl source materials.

Experiments in the growth of HgCdTe on CdTe have been focussed on HgTe layers, since this is the most difficult component to grow. Layers of considerably improved morphology are now being grown, by paying careful attention to the establishment of the proper pre-growth conditions, and to the arrival rates of the respective Hg and Te species.

Sample evaluation is presently carried out by the measurement of Hall effect to 10K, and by IR transmission. In addition, photoluminescence is being extensively used on CdTe layers grown on this program. Some SIMS analyses of the grown layers has been undertaken as well, through colleagues at the General Electric Company.

Double crystal x-ray diffractometer system has been ordered on another program. This will also be used to evaluate our material, once it is installed.

PAPERS AND PRESENTATIONS

A number of papers, based on our work, have been submitted to the professional journals. These are listed, together with their current status. In addition, presentations on this work have been made to DARPA and also at professional society meetings. Full length versions of the papers are attached as an Appendix to this report.

PUBLICATIONS:

1. P.M. Raccah et al, and S.K. Ghandhi, I. Bhat, "Study of MCT Epilayers Grown by Metalorganic Vapor Phase Epitaxy", J. Appl. Phys. 57(6), 2014 (1985).

2. S.K. Ghandhi, N.R. Taskar, I.B. Bhat, "Growth of CdTe on GaAs by Organometallic Vapor Phase Heteroepitaxy", Appl. Phys. Lett. 47(7), 742 (1985).

3. I.B. Bhat, S.K. Ghandhi, "Growth and Properties of $Hg(1-x)Cd(x)Te$ on GaAs Substrates", J. Appl. Phys. 59(6), 2253 (1985).

4. I.B. Bhat, S.K. Ghandhi, "The Growth of Mercury Cadmium Tellurice by Organometallic Epitaxy", J. Crys. Growth (accepted).

5. I.B. Bhat, N.R. Taskar, S.K. Ghandhi, "The Organometallic Heteroepitaxy of HgCcTe on GaAs Substrates", J. Vac. Sci. Tech. (accepted).

6. I.B. Bhat, S.K. Ghandhi, "On the Mechanism of Growth for the OMVPE of CdTe", J. Electrochem. Soc. (submitted).

PRESENTATIONS:

1. S.K. Ghandhi, "The MOCVD of II-VI Compounds", Workshop on Gigabit Computing, Stuttgart, Germany, Apr. 15-16, 1985.

2. I.B. Bhat, S.K. Ghandhi, "Growth of Hg(x)Cd(1-x)Te on CdTe Substrates by Organometallic Epitaxy", Second Biennial OMVPE Workshop, Cornell, NY , Aug. 1-2, 1985.

3. I.B. Bhat, N.R. Taskar, S.K. Ghandhi, "The Growth of HgCdTe on GaAs Substrates by Organometallic Epitaxy", 1985 Workshop on the Phys. and Chem. of Mercury Cadmium Telluride, San Diego, CA.

4. I.B. Bhat, S.K. Ghandhi, "Growth and Characteristics of Hg(1-x)Cd(x)Te on CDTe Substrates", Materials Reserach Society Mtg., Boston, MA, Dec. 2-7, 1985.

WORK PLANNED FOR THE SECOND YEAR

A major task of the second year will be the completion of the new epi-reactor, and bringing it into full operation. Here, the emphasis will be on learning to use this machine, and in adjusting system parameters for suitable growth. In addition, we expect continuing work on all phases of the growth and evaluation studies.

A second important area is the fabrication and evaluation of cevice structures made on these materials. The fabrication of these structures, as well as the cevelopment of test methods, will be investigated. An additional studer: has been hired to work full time on this aspect of the program.

New analytical methods will also be explored; with this in mind, a double crystal X-ray diffractometer system has been placed on order (on another program). This will be used to evaluate our material once it is in operation.

Finally, new avenues of research will be explored when and if the opportunity arises. In our opinion, an important feature of this program is the flexibility provided to do so, if they appear promising.

APPENDIX

Study of mercury cadmium telluride epilayers grown by metalorganic vapor-phase epitaxy

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We report on the growth and characterization of HgCdTe epilayers grown by metalorganic vapor-phase epitaxy. The transport properties indicate that it is possible to grow epilayers with mobilities comparable to those of the best bulk-grown materials. Electrolyte electroreflectance studies have yielded depth profiles for the alloy composition, the strains, and the density of polarizable defects. These latter results indicate very clearly that the interface alloy/substrate is very sharp and does not extend over more than 2000 Å. Moreover, in the bulk of the epilayers the strains are low and comparable to those found in high-quality bulk single crystals.

INTRODUCTION

It has been found historically in the growth of III-V materials that epitaxial growth techniques have been able to improve on the main bulk, single-crystal growth technique, which is liquid-encapsulated Czochralski (LEC). Although the first epitaxial approach was liquid-phase epitaxy (LPE), metalorganic vapor-phase epitaxy (MOVPE), and molecular-beam epitaxy (MBE) now vie for dominance of the field.

Such, however, has not been the case[1] for the growth of $Hg_{1-x}Cd_xTe$, for which LPE has remained a relatively poor second to the two main bulk single-crystal growth techniques, which are solid-state recrystallization and modified Bridgman. It is only very recently[2] that LPE growth on Zn-doped CdTe substrates has given indications of real progress and of the possibility of reaching bulk quality, an outcome which is still in the future. It was therefore most reasonable to attempt the exploration of MOVPE growth. The pioneering work of J. B. Mullin *et al.*[3] met with limited success in producing materials with acceptable mobilities. Secondary ion mass spectroscopy studies[4,5] seemed to indicate that at least part of the difficulty resulted from residual impurities.

Meanwhile J. P. Faurie *et al.*[6] in a remarkably fast development, produced MBE materials exhibiting transport properties competitive with those of the best bulk single crystals. In fact, they went even further and prepared the first[7] 'true' II-VI superlattices. This latter accomplishment implied the existence of very sharp interfaces between CdTe and HgTe, a fact which has now been confirmed[8]

More recently, some of us[9,10] have reported on new and most encouraging developments in the MOVPE growth of HgTe and $Hg_{1-x}Cd_xTe$ epilayers. We report here for the first time transport and electrolyte electroreflectance (EER) results which show that MOVPE materials can now be grown with properties very close to those reported for bulk or MBE materials.

EXPERIMENT

A. Growth procedure

The epitaxial growth technique has been reported in an earlier paper[11] and will only be briefly summarized here.

Epitaxial MCT was grown at atmospheric pressure in a quartz horizontal reactor tube using hydrogen as the carrier gas. Mercury vapor was transported to the reaction zone by passing hydrogen over heated mercury. Diethyltelluride (DETe) and dimethylcadmium (DMCd) obtained from Alfa Products, Danvers, MA., were used as metalorganic sources of Te and Cd, respectively. These were introduced in vapor form by bubbling hydrogen through the respective bubblers, which were held at 15 °C. Growth was carried out on an rf-heated graphite susceptor held at 415 °C. In addition, the tube wall in front of the susceptor was heated by a separate resistance heater to prevent mercury condensation.

The substrates used for epitaxial deposition were (100) oriented 3° towards (110) CdTe wafers. These were degreased in organic solvents and etched in a 2% Br-methanol solution. This treatment resulted in a highly polished surface.

Growth was carried out with a total hydrogen flow of 11/min, a DETe partial pressure of about $2.5 \cdot 10^{-3}$ atm, a DMCd pressure of about $7 \cdot 10^{-5}$ atm, and a mercury partial pressure of 0.04 atm. The composition of the layers was controlled by changing the partial pressure of the DMCd and DETe. This was achieved by changing the flow of hydrogen in the appropriate bubblers. Growth was terminated by shutting off the Cd and Te sources and cooling down to 150 °C in mercury vapor. The flow of mercury vapor in the reactor was then terminated and the layer brought down to room temperature.

B. Transport measurements

Hall and resistivity measurements were made as a function of temperature by means of the Van der Pauw method, with a magnetic field strength of 2.1 kG. A clover-shaped pattern was delineated for this purpose, and contacts were made using silver epoxy. No alloying of the contacts was necessary in order to obtain good ohmic contact.

We show in Fig. 1 the Hall mobility versus temperature data for one of the samples of nominal Cd concentration $x = 0.19$. The maximum value of the mobility is of the order $3 \cdot 10^5$ cm^2/V sec for this sample and occurs at about 60 °K, below which the mobility falls, indicating that impurity scattering dominates in this region.
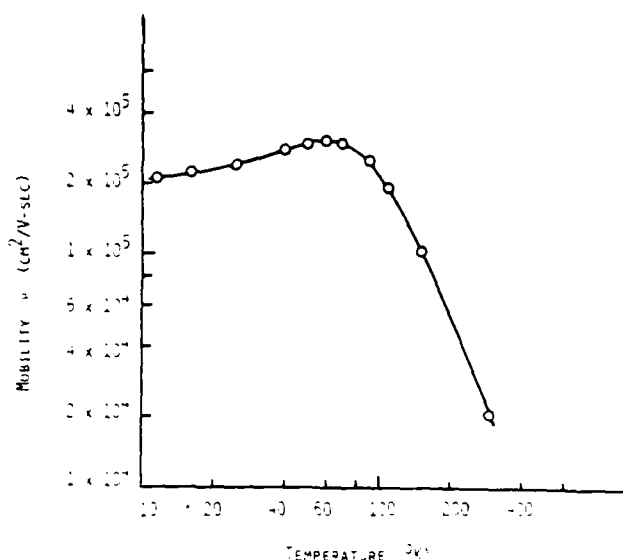
FIG. 1. Mobility vs temperature for a $Hg_{0.81}Cd_{0.19}Te$ layer grown on a CdTe substrate.

We show in Fig. 2 the Hall coefficient $(R_H = 1/nq)$ versus temperature. Classical n-type behavior is observed down to 11 °K, with no carrier freeze out and an extrinsic R_H value of 3670 cm³/C. This corresponds to n-type conduction with a carrier concentration of 1.7×10^{15} cm⁻³. The R_H value is constant below 50 °K, in the extrinsic region. No change in the R_H value was observed when the magnetic field was increased to 4.5 kG, indicating that p-type conduction is negligible.

Transport measurements were made on many samples grown under identical growth conditions, and we have consistently observed mobilities in excess of 2×10^5 cm²/V sec for EER measured x values of 0.2 at 77 °K.
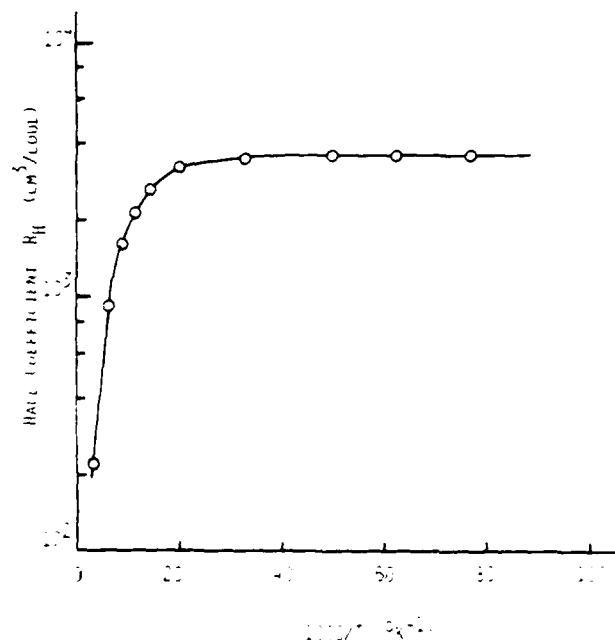
FIG. 2. Hall coefficient vs temperature for the layer of FIG. 1.

C. EER results

EER has been used extensively to study the variations in composition laterally[11] and in depth[1] of pseudobinary alloys and in particular $Hg_{1-x}Cd_xTe$. More recently we have shown[2] that EER can be used to study defects in semiconductors because the modulating electric field E couples to the two main categories of defects, which are long-range strains and polarizable defects. These interactions, which had been considered negligible in all previous theoretical treatments, give rise to two additional signals, one of which is proportional to a first derivative and the other to a second derivative of the dielectric function with respect to energy. The experimental EER spectrum is then a linear combination of these first- and second-derivative line shapes with the conventional third-derivative line shape[12] (TDL).

In our generalization of the original theory of Aspnes[12] we introduced the effect of defect scattering in the same way as he did in a later paper,[13] following the work of Lukes and Somaratna,[14] who first introduced the quantity σ^2 which measures the strength of defect- and impurity-induced scattering. Otherwise we followed exactly the original approach of Aspnes, except that we did not neglect terms proportional to the small shifts, ΔE_j and $\Delta\sigma^2$, in the critical energy and in σ^2. In particular, we made the same low-field expansion as Aspnes to obtain the generalized result,

$$\Delta\epsilon_j = C_{oj}E^{-2}[(\hbar\Omega_j)^3 d^3/dE^3$$
$$+ 6\Delta\sigma^2 d^2/dE^2 - 3\Delta E_j d/dE]E^2\epsilon(E), \qquad (1)$$

for the contribution of the jth interband transition of $\Delta\epsilon$, where C_{oj} is a constant, E is the energy, $\hbar\Omega_j$ is the average energy gained by an optically excited electron from the field E and is of order 10 meV, and $\epsilon(E)$ is the dielectric function. Still following the original treatment and making a parabolic-band approximation, we found for the three-dimensional critical points E_1 and $E_1 + \Delta_1$, the generalized functional form (GFF)

$$L(E) = C_j[(\hbar\Omega_j)^3 L(E,5/2) - 4\Delta\sigma^2 L$$
$$\times (E,3/2) - 4\Delta E_j L(E,1/2)], \qquad (2)$$

for the EER line shape, where

$$L(E,n/2) = \cos(\theta_j - n\Phi_j/2)/[(E - E_j)^2 + \Gamma_j^2]^{n/4} = L_n, \qquad (3)$$

with Γ_j being a phenomenological broadening parameter and with $\phi_j = \tan^{-1}[\Gamma_j/(E - E_j)]$. Here, C and θ have a weak dependence on energy, which is easily taken into account by introducing the Seraphin coefficients.[15] That energy dependence is, however, usually ignored because the evaluation of the Seraphin coefficients requires an independent knowledge of the real and imaginary parts of the dielectric function and because neglecting it only affects the determination of the parameter θ, leaving E and Γ essentially unaffected.

It is apparent that the GFF reduces to the conventional functional form for the TDL upon setting ΔE and $\Delta\sigma^2$ equal to zero, with L_5 being proportional to the TDL. For $n = 1$ and $n = 3$, L_n is proportional to the first and second derivatives, respectively, of the same linear combination of ϵ_1 and ϵ_2 as occur in the TDL. It is clear that L_1 and L_3 have qualitatively different shapes from the TDL and from one another.
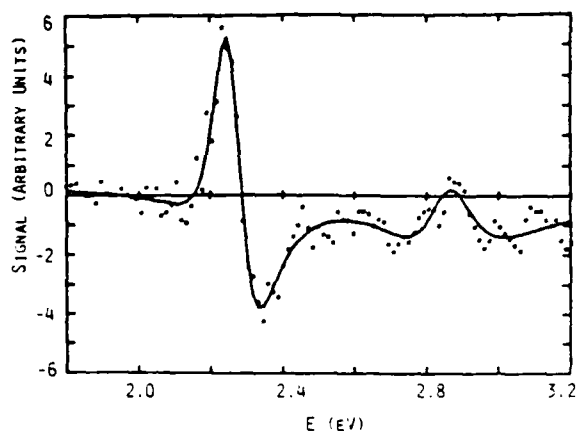
FIG. 3 Fit of the theory to the EER data obtained on a typical MOVPE sample after removing 0.3 μm. This example is representative of all our results on MOVPE samples. The EER signal on an arbitrary scale is displayed vs photon energy in eV. The continuous line is computed from the theoretical expression and the values of the parameters are listed in the first line of Table I.

In addition to allowing the determination of the interband transition energy E_i, the phase θ_j and the broadening parameter Γ_j, the GFF allows the determination of the ratios of the two defect-related quantities, ΔE_i and $\Delta \sigma^2$, to $(\hbar\Omega_i)^3 = e^2 E^2 \hbar^2 / 8\mu$, the average energy gained by the optically excited electrons from the modulating field E. One of these quantities ΔE_i results primarily from the electrostrictive coupling of E to long-range strains, and the other $\Delta \sigma^2$ arises from the polarization of charged polarizable defects, whereas the value of $\hbar\Omega_i$ is independent of defects and is very nearly the same for all $Hg_{1-x}Cd_xTe$ samples.

TABLE I. Profile of a typical $Hg_{1-x}Cd_xTe$ epilayer.

D	E_i(eV)	τ	Γ(eV)	$\dfrac{\Delta E_i}{(\hbar\Omega_i)^3}$ eV^{-3}	$\dfrac{\Delta\sigma^2}{(\hbar\Omega_i)^3}$ eV^{-1}
0.29	2.262	0.178	0.087	-4.4	-0.9
0.39	2.263	0.179	0.090	1.5	-1.5
0.49	2.258	0.174	0.091	-0.7	-1.8
0.78	2.268	0.185	0.093	-6.6	-1.3
0.88	2.262	0.178	0.082	-8.6	-2.0
1.08	2.268	0.185	0.105	-15.2	0.1
1.28	2.260	0.176	0.111	-4.2	-0.7
1.38	2.263	0.179	0.104	-11.1	-1.8
1.47	2.269	0.186	0.102	-4.1	-1.5
1.57	2.275	0.193	0.105	-2.8	-1.5
1.68	2.276	0.194	0.096	-1.5	-1.2
1.77	2.283	0.203	0.091	-0.2	-1.6
1.96	2.282	0.202	0.101	-3.5	-1.1
2.26	2.291	0.213	0.096	13.3	-1.8
2.36	2.278	0.197	0.094	-2.3	-1.8
2.45	2.286	0.206	0.095	-1.9	-1.7
2.55	2.295	0.217	0.099	-0.6	-1.1
2.65	2.294	0.216	0.099	-4.0	-1.3
2.84	2.341	1.0	0.077*	104.5*	0.8*
2.94	2.333	1.0	0.126	-15.3	1.9
3.04	2.360	1.0	0.090	-103.0	7.4
3.14	2.405	1.0	0.103	-67.6	2.5

* These values are less certain than the others because the minimum in the fit was very broad in this case.

We have carried out a full EER study of several MOVPE epilayers. In each case we have repeatedly removed, by careful etching, approximately 1000 Å and have measured the EER spectrum after each etch. This procedure, which was developed and reported earlier, allows us to profile[1] the properties of a given layer.

DISCUSSION

The fit of the theory to a typical spectrum is shown in Fig. 3. The critical points at E_1 and $E_1 + \Delta_1$ were fit simultaneously. We also summarize in Table I the profile of a typical epilayer. The effect of background signals due to the long tails of the first-derivative L_1 line shapes from other critical points was taken into account using several different methods, with the different methods yielding very similar results in all cases. The uncertainties in our values for the interband transition energy E_1, the alloy composition x, the broadening parameter Γ, and the two new parameters $\Delta E_1/(\hbar\Omega_1)^3$ and $\Delta\sigma^2/(\hbar\Omega_1)^3$ are estimated to be approximately ± 5 meV, ± 0.006, ± 3 meV, ± 7 eV^{-2}, and ± 0.5 eV^{-1}, respectively. These quantities are given as a function of depth D in microns.

There are three main regions in the epilayer: (1) the surface region down approximately $1.5\,\mu m$, (2) the bulk, extending approximately over the next $1.3\,\mu m$, and (3) the substrate, where the alloy composition is obviously $x = 1$.

In terms of these regions, three main features are conspicuous in Table I. The first is that the alloy composition x is different in the surface region than in the bulk of the layer. The second is that the parameters ΔE_1 and Γ take on somewhat larger values in the transition region between the surface region and the bulk of the layer. Finally, the interface between the epilayer and the substrate is quite abrupt and exhibits dramatic changes in the values of Γ, ΔE_1, and $\Delta\sigma^2$. Let us now examine these features in more detail, beginning with the first.

As for most epilayers, except for those produced by MBE, the value of the alloy composition x is lower near the surface than in the bulk of the layer indicating that the surface is rich in mercury. This is due here to the fact that after interruption of growth the samples must be cooled from the growth temperature of about 400 °C down to 150 °C in an overpressure of mercury to avoid thermal decomposition. Hence, a top surface enriched in mercury is to be expected and results from in-diffusion from the mercury ambient.

As can be seen, the narrow etching steps which we have used have allowed us to determine with excellent resolution that the depth of this enriched zone is $1.5\,\mu m$. Given the annealing temperature and the known Hg pressure in the reactor, it is possible to estimate[5] the depth of mercury diffusion during this fortuitous "anneal." The estimate is of approximately $1\,\mu m$ and is in reasonable agreement with the observed depth of $1.5\,\mu m$.

The second important feature is that in the transition region from 1 to 1.6 μm depths, ΔE_1 and Γ assume larger values than those found nearer the surface or in the more uniform region below. This clearly shows that the rapid gradient in mercury concentration x found in this region is associated with long-range strains, which enhance ΔE_1, and al-

loy disorder, which enhances Γ. This rather remarkable result is consistent with our earlier conclusions[1] that mercury-diffused, n-type material is likely to be more strained than the original p-type material. On the other hand, very near the surface, for D less than 1 μm, Γ is seen to be similar by almost 0.01 eV than it is in the bulk, which is apparently contradictory. However, this can be explained by the smaller Cd concentration x in the top region. It is well known that alloy disorder contributes substantially to the value of Γ. Furthermore, both the spatial fluctuation of local band energies and the width of alloy band spectral-weight functions[17] increase approximately as $[x(1 - x)]^{0.5}$ with increasing alloy composition x. We find that the observed decrease in Γ within 1 μm of the original surface is entirely consistent with the theoretical estimate of this effect.

As can be seen, the bulk region is remarkably uniform in alloy composition x. In addition, the low values of both ΔE_1 and $\Delta\sigma^2$ indicate that this part of the layer is only weakly strained and has few polarizable defects. Also the parameter Γ, which describes the magnitude of the random potential fluctuations associated with alloy disorder, varies very little over this region. Moreover, the root-mean-square deviation from the average composition of $x = 0.21$ is less than 0.01, which is comparable to or better than that of the best LPE epilayers. This result is particularly remarkable when compared to that typically found in LPE materials.[2] There the epilayer/substrate interface, which is heavily graded and very rich in defects, is typically 5 μm deep, so that thin layers (less than 5 μm) grown by this technique would be of poor quality. When grown by MOVPE instead, a thin layer is both uniform and of high quality. This is because in MOVPE material the interface itself is remarkably abrupt, certainly less than 0.2 μm thick, and the properties of the epilayer hardly change until the very transition to the substrate.

The last remarkable feature is the huge jump in strain at the interface accompanied by a double change in the sign of ΔE_1. This jump in strain is accompanied by a change in the sign and an increase in the magnitude of $\Delta\sigma^2$. A simple explanation for the behavior suggests itself: it is that the CdTe substrate is Hg diffused during the early stages of the growth, and that here too the mercury diffusion induces strains which yield large negative contributions to ΔE_1, but that there is an additional, ever larger, strain localized at the surface of the substrate which has the opposite effect on ΔE_1. This localized strain may result from a lattice mismatch at the surface of the substrate; it clearly has a symmetry different from that of diffusion-induced strains, so it is not too surprising that it has the opposite effect on ΔE_1.

This explanation, if correct, would speak strongly against another common growth technique, the vapor-phase epitaxy technique, because that technique makes use precisely of such a process. Our results would indicate that such an approach is bound to produce graded and strained materials,

with the intensity of the strains reaching into the plasticity range and becoming associated with extended defects, as is in fact commonly found. The high mobilities reported for these materials are misleading, being due to the compositional gradient, and reflecting chemical inhomogeneities rather than the quality of the material.

Still consistent with the above explanation, the density of polarizable defects increases sharply in the interface region, possibly indicating the formation of extended defects as has already been seen in LPE materials.[2] Finally, $\Delta\sigma^2$ changes sign near the interface, a fact which indicates that the application of the modulating electric field now increases, rather than decreases, the scattering of carriers by the polarizable defects in the substrate.

CONCLUSIONS

We have shown that MOVPE is a promising technique for the growth of device quality $Hg_{1-x}Cd_xTe$. The transport properties of the material are comparable to those of bulk single crystals, and EER profiling shows that the control of composition is good if one disregards the surface's mercury enrichment. The power of the new EER line-shape analysis has been demonstrated by its revealing the effects of mercury in-diffusion at the top of the epilayer and by the information it gives about the interface region.

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Growth of CdTe on GaAs by organometallic vapor phase heteroepitaxy

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Organometallic vapor phase heteroepitaxy of CdTe on (100) oriented GaAs substrates is described in this letter. It is shown that high quality CdTe layers can be grown on GaAs substrates over the temperature range 350–440 °C by this process. Growth under different temperatures and reactant partial pressures is described. Conditions are outlined for obtaining optimum photoluminescence properties, with suppression of the defect level associated with the cadmium vacancy. Electron channeling data are presented to indicate that excellent epitaxy is achieved by this process. The orientation of the epitaxial layer is found to be the same as that of the substrate.

Cadmium telluride is an important semiconductor material for use in solar energy conversion. It is also a natural choice as a substrate material for the epitaxial growth of $Hg_{1-x}Cd_xTe$, because of their close lattice match and chemical compatibility. Unfortunately, bulk CdTe is a difficult material to grow, so that its crystal quality is generally poor compared to what would be expected on theoretical considerations.[1] Indium antimonide substrates, which are closely lattice matched to CdTe, have been investigated[2-4] for this reason. In a previous letter[4] we have shown that organometallic vapor phase epitaxy (OMVPE) can be used for the growth of CdTe layers on this substrate material. Both n-type and semi-insulating CdTe layers were grown by this technique. These layers were shown to be electrically

superior to those grown on bulk CdTe, as evidenced by a band edge photoluminescence peak which is typically two decades larger than that obtained with layers grown autoepitaxially on CdTe, under identical growth conditions.

A disadvantage of using InSb as a substrate material is its relatively low energy gap (0.228 eV at 77 K). This renders it optically opaque at wavelengths below 5 μm, so that it is an unsuitable substrate material for many back-illuminated photodetector applications. As a result, attention has focused on the use of GaAs as an alternate substrate material because of its wider energy gap (E_g = 1.51 eV at 77 K). A large lattice mismatch ($\simeq 14\%$) is present between GaAs and CdTe (the lattice constant of GaAs is 5.653 Å at 27 °C as compared to 6.482 Å for CdTe). Nevertheless, epitaxial

growth of high quality CdTe layers on GaAs substrates was found to be possible by molecular beam expitaxy (MBE). Epitaxial growth of both (100) CdTe on (100) GaAs[5,6] and (111) CdTe on (100) GaAs[7,8] has been reported for this approach.

Growth of CdTe films on (100) GaAs by OMVPE has been reported[9] but no details of the experimental conditions are available. This letter reports the preparation of large area, high quality CdTe films on (100) GaAs by OMVPE and the results of photoluminescence (PL) measurements and electron channeling patterns taken on the epilayers. These layers have featureless morphology, and are shown to be comparable in electrical quality to those grown lattice matched on InSb substrates, and considerably superior to those grown autoepitaxially on CdTe substrates.

Epitaxial growth of CdTe was carried out in a system described elsewhere.[4] GaAs substrates of (100) misoriented $2°\rightarrow(110)$ were cleaned in organic solvents and etched in Caro's etch ($H_2SO_4 : H_2O_2 : H_2O = 5 : 1 : 1$ by volume) for 10 min to remove 15–20 μm prior to epitaxial growth. After loading the substrates, the system was purged with nitrogen gas and brought up to the growth temperature in hydrogen gas.

Growth was carried out over the 350–440 °C temperature range. The partial pressure of DMCd was varied from 1 to 7 · 10^4 atm. whereas the partial pressure of DETe was varied from 3 to 10 × 10^{-4} atm for growth runs over this temperature range. Runs were terminated by turning off the reactants and the rf power, and simultaneously increasing the hydrogen flow to 3 slm in order to effect a rapid cool down. Samples were removed from the reactor when the substrate temperature fell below 100 °C.

The growth rate was found to be sublinear, as a function of P_{DMCd} (with P_{DETe} held constant), and also sublinear as a function of P_{DETe} with P_{DMCd} held constant. We believe that this can be explained by invoking a Langmuir–Hinshelwood model for the growth, with adsorption and desorption as the two competing processes for both the species arriving on the slice. Details of this model will be published at a later date.

Figure 1 shows a photograph of a 2.5-μm-thick large area sample. Typically, layers of this type were specular in character, with edge to edge flatness over the grown layer. The morphology of these layers is shown in Fig. 2, and indicates a complete absence of surface features. Excellent layer morphology was experienced over the full temperature range; however, the range of partial pressures of DMCd and DETe for which this could be achieved had to be optimized for each growth temperature. The achievement of good morphology became increasingly difficult at higher growth temperatures (440 °C). We believe that this is due to the tendency of tellurium crystallites to form on the substrate at these temperatures. It is probable that three-dimensional growth, initiated by nucleation at these sites, leads to a deterioration in the morphology. An alternative possibility is the formation of a solid methylene polymer[10] at these temperatures, which would have the same consequence.

Electron channeling studies were undertaken to investigate the crystalline quality and orientation of the grown layer. This technique is preferable to x-ray diffraction for thin epitaxial layers, since it has a depth resolution of under 500 Å, whereas that of x-ray diffraction ranges from 5 to 10 μm. Typically, the grown layer in our experiments was about 2.5 μm thick. Figure 3(a) shows the electron channeling pattern for a GaAs substrate for a scan angle of 9°, and is typical for (100) oriented material. The electron channeling pattern for a 2.5-μm CdTe layer, grown at 350 °C on an identical substrate, is shown in Fig. 3(b). Here, the pattern is replicated with almost the same line sharpness, indicating the excellent crystal quality of the CdTe. The difference in crystal parameter, about 14%, is directly seen in the change in pattern dimensions for (200) reflections. (Both sets of patterns are reproduced at the same magnification.) Finally, the grown layer is seen to be of (100) orientation from Fig. 3(b); i.e., it follows the substrate orientation. The orientation of the layers grown at other temperatures was also confirmed to be (100) by observing Laue back-reflection photographs, which also showed fourfold symmetry. This result is in contrast to the findings of workers with MBE[5-7] where the growth of
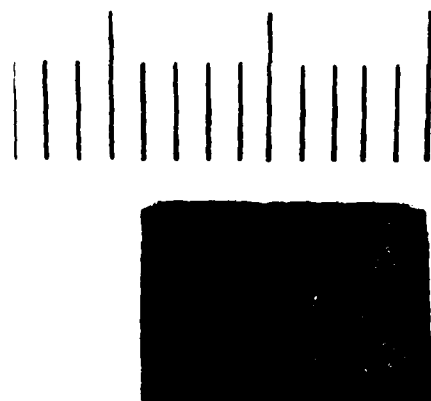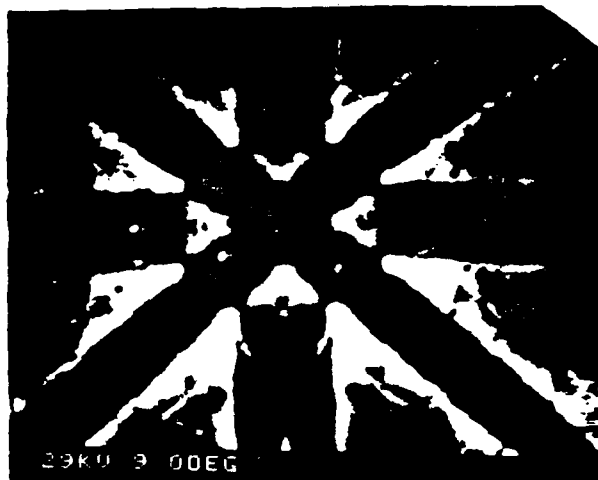

25 μm

(a)

(b)

FIG. 3. Electron channeling pattern for (a) a (100) GaAs substrate and (b) a CdTe epilayer grown on a (100) GaAs substrate. The scanning electron microscope was operated in the specimen current mode for these figures.
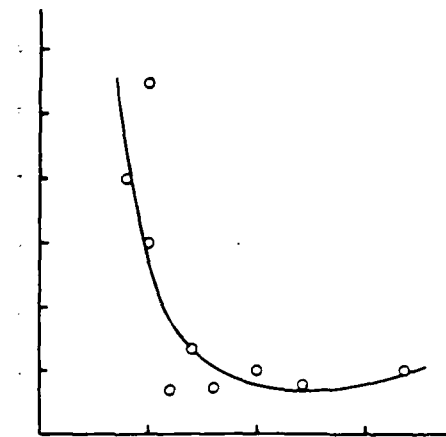

FIG. 4. Ratio of the intensity of the Cd vacancy-donor complex defect peak to the band edge peak, plotted as a function of P_{DMCd}/P_{DETe}.

both (100) and (111) CdTe has been reported on (100) GaAs substrates.

Films grown by this process were found to be semi-insulating. Photoluminescence (PL) measurements were made on them at 77 K using a 7-mW He-Ne laser as the optical excitation source. The PL spectra showed a band to band peak at 1.58 eV, and a second peak at 1.43 eV which has been established to be due to the Cd vacancy-donor complex.[11] The ratio of the intensities of these peaks is often used as a measure of the device quality of CdTe layers. Although this quantity is also related to system factors such as the laser intensity[12] it is useful for comparing films with similar surface morphology, if they are tested under a similar set of measurement conditions. Figure 4 shows the ratio of the intensity of the defect peak to the band edge peak (I_{Cd}/I_{BE}) as the function of the P_{DMCd}/P_{DETe} ratio for a typical set of growth runs. This intensity ratio falls with increasing P_{DMCd}/P_{DETe}, as expected. A broad minimum, around 0.5, is seen to occur for a P_{DMCd}/P_{DETe} ratio of unity. It should

be emphasized, however, that the P_{Cd}/P_{Te} ratio is not the same as the P_{DMCd}/P_{DETe} ratio. The occurrence of the minimum at unity is fortuitous and is related to system parameters such as susceptor and reaction chamber dimensions, which affect the preheating of the reactant species before arrival at the GaAs substrate. The existence of a broad minimum *does* indicate, however, that a wide range of organometallic flow ratios can be used without deteriorating the electro-optical parameters of the grown layer.

In summary, we have shown that large area, single crystal CdTe layers of excellent morphology can be grown on (100) GaAs substrates. The orientation of the layers was identical to the substrate orientation. Electron channeling measurements have shown that these layers are of excellent crystalline quality. The electrical quality of these layers has been demonstrated by PL measurements, and conditions are presented for minimizing the cadmium-vacancy defect level. Finally, the layers were semi-insulating in character. Thus, they serve as a starting point for the subsequent growth of $Hg_{1-x}Cd_xTe$ films, which would be electrically isolated from the lattice-matched CdTe buffer layer and the semi-insulating GaAs substrate.

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Growth and properties of $Hg_{1-x}Cd_xTe$ on GaAs substrates by organometallic vapor-phase epitaxy

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Growth of epitaxial mercury cadmium telluride ($Hg_{1-x}Cd_xTe$) on (100) GaAs substrates by organometallic vapor-phase epitaxy is described. Transport measurements made on these layers at 80 K indicate an electron mobility greater than 2×10^5 cm²/ V s for layers of composition $x \cong 0.2$. An intervening CdTe buffer layer was used to accommodate the large (14%) lattice mismatch between these systems, and HgCdTe layers have been grown with CdTe buffer layer thicknesses from 1000 Å to 3 μm. It is shown that a CdTe buffer layer of 2–3 μm is necessary to accommodate the misfit dislocations at the CdTe-GaAs interface.

$Hg_{1-x}Cd_xTe$ (MCT) is an important intrinsic semiconductor material for infrared detector applications, especially in the 8–16 μm range. Epitaxial growth of this material on a suitable substrate has received considerable attention in the past few years. CdTe is a natural choice as a substrate material because of its excellent lattice match and chemical compatibility with MCT systems. However, the lack of availability of high-quality, large-area CdTe substrates prompted many workers to consider alternate substrates such as GaAs, InSb, and sapphire. Of these, GaAs is especially important because it can serve as a window for backside illuminated devices. Moreover, its use opens up the possibility of integrating GaAs circuits with sensor devices of HgCdTe in a monolithic structure.

The growth of CdTe and MCT on GaAs substrates by molecular-beam epitaxy[1,2] (MBE) and organometallic vapor-phase epitaxy[3,4] (OMVPE) has been the subject of study in recent papers. In addition, we have reported on the electron channeling patterns and photoluminescence properties of CdTe grown on GaAs[5] by OMVPE. Our work has shown that, although the lattice mismatch between CdTe and GaAs is about 14%, high-quality single-crystal layers with featureless morphology could be obtained over the 350–420 °C range of growth temperatures. As an extension of this work, we report for the first time on the electrical characterization of MCT layers grown on GaAs substrates by OMVPE. These are grown with an intermediate buffer layer of CdTe in a continuous process. The effect of CdTe buffer layer thickness on the electrical properties of the MCT layer will also be discussed.

The epitaxial growth of CdTe and MCT was carried out in a system described previously.[5] Dimethylcadmium
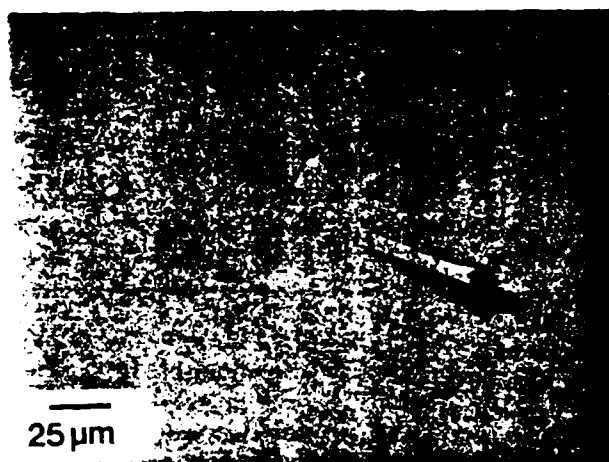
FIG 1 Morphology of a HgCdTe layer grown on (100) GaAs substrate with a 0.2-μm-thick CdTe buffer layer.

FIG. 2. Electron mobility μ in HgCdTe as a function of temperature. The composition is $x \approx 0.2$ and the layer was grown with a 2.6-μm-thick CdTe buffer layer.

(DMCd) and diethyltelluride (DETe), held at 15 °C, were used as the cadmium and tellurium sources, respectively, and elemental mercury was used as the mercury source.

Semi-insulating GaAs substrates of (100) 2°→(110) orientation were cleaned in organic solvents and etched in Caro's etch (H_2SO_4:H_2O_2:H_2O = 5:1:1 by volume) for 10 min to remove 15–20 μm prior to epitaxial growth. After loading the substrates, the system was purged with nitrogen and brought up to the growth temperature in hydrogen.

First, a layer of CdTe was grown on GaAs; typically, partial pressures of $1-7 \times 10^{-4}$ atm were used for the DMCd, and $3-10 \times 10^{-4}$ atm for the DETe. Growth temperatures were in the range of 350–440 °C. Specular surfaces of CdTe were obtained for these conditions. After the growth of the CdTe buffer layer, the MCT layer was grown at a substrate temperature of 415 °C, without opening the reactor system. To do this, the reactor wall and the mercury chamber were brought up to the required temperatures (230 and 300 °C, respectively). The susceptor was heated to 415 °C in a DMCd ambient to prevent the decomposition of CdTe, and MCT growth was initiated by turning on the Hg and DETe flows.

Figure 1 shows the morphology of a MCT layer grown on GaAs, with a 0.2-μm-thick CdTe buffer layer. The layer is mirrorlike to the unaided eye, but a small number of hillocks (about 500/sq cm in number) are visible when viewed under the microscope. MCT layers grown on bulk CdTe substrates under identical conditions do not result in such hillocks, indicating that they probably originate during the growth of CdTe buffer layers. The composition of these hillocks was checked by energy dispersive x-ray analysis and was found to be identical to the composition of the surrounding layer. It is well known that HgTe grows much faster near defects or sample edges because these provide easy nucleating sites. Hence, any defect or kink site on the CdTe epilayer will show up as a hillock in the MCT layer. Such defects can be expected to occur in the form of stacking faults because of the large lattice mismatch between CdTe and GaAs.

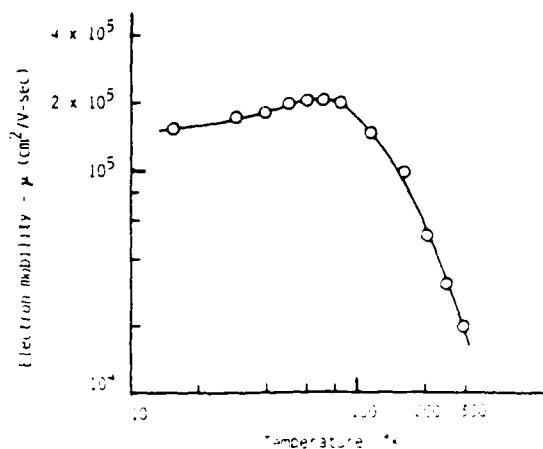Hall and resistivity measurements were made from 10 to

300 K by means of the Van der Pauw method, with a magnetic field strength of 2.1 kG. A cloverleaf-shaped pattern was delineated in the layer to avoid errors due to poor contact placement. Indium solder was used for the contacts in all these measurements.

Figure 2 shows the Hall mobility versus temperature data for a MCT layer of composition $x \cong 0.2$. This layer was grown with a CdTe buffer layer thickness of 2.6 μm, and had a MCT layer thickness of 5.6 μm. The maximum value of the mobility for this layer is 2.1×10^5 cm^2/ V s at 80 K.

Figure 3 shows the Hall coefficient (R_H) as a function of inverse temperature for the layer shown in Fig. 2. From the value of R_H at low temperature, the carrier concentration in this layer is estimated to be approximately 2.3×10^{15} cm^{-3}.
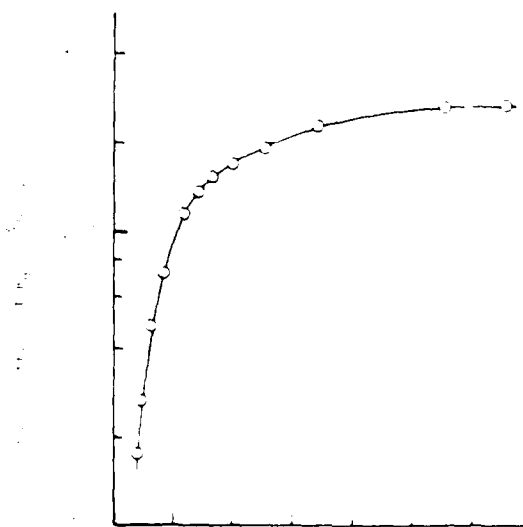

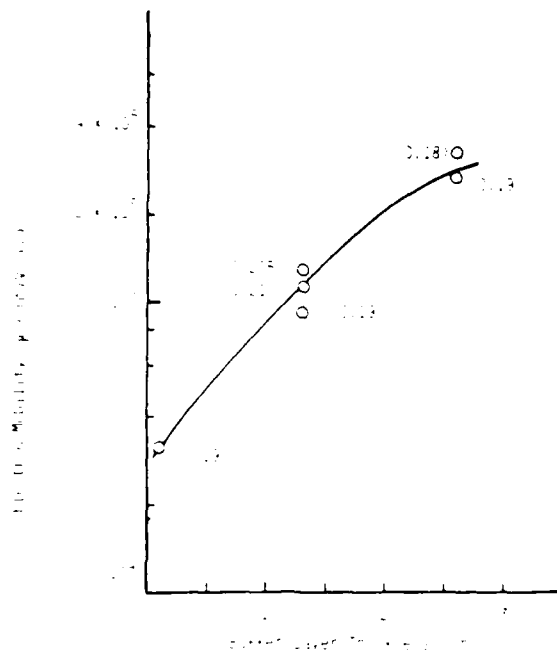FIG 3 Hall coefficient vs reciprocal temperature for the layer of Fig 2

FIG 4 Electron mobility at 80 K in HgCdTe layers, as a function of CdTe buffer layer thickness. The composition x is shown in the parentheses.

between GaAs and CdTe systems, and give layers with a large value of Hall mobility, and low carrier concentration.

Experimentally, a misfit dislocation density of about $10^9/cm^2$ has been observed[9] for the CdTe-Hg$_{0.8}$Cd$_{0.2}$Te interface. On the other hand, dislocation densities of 10^{11}–$10^{12}/cm^2$ have been reported for the CdTe-GaAs interface. The use of a buffer layer thus has the potential for effecting a 2–3 decade reduction in this dislocation density. Transmission electron microscopy studies done on CdTe layers grown on GaAs have shown[7,9] that a 2–3 μm layer is sufficient for this purpose. This study supports the above view from measurements of the transport properties.

In summary, the OMVPE growth of MCT layers, grown on GaAs substrates, with an intermediate buffer layer of CdTe, was demonstrated. Except for the presence of few hillocks, the morphology of the layers was featureless. The transport properties of these layers were reported for the first time, and their high quality established by this data. These electrical measurements have confirmed that the misfit stress between GaAs and CdTe is accommodated between 2 and 3 μm from the CdTe/GaAs interface.

The effect of the buffer layer thickness on the properties of the MCT layers was also studied. Figure 4 presents the electron mobility at 80 K for a number of MCT layers with x in the 0.18–0.21 range. All layers were grown under identical conditions except that the thickness of the CdTe film was varied. We note that the thickness of the buffer layer has a strong effect on the electron mobility in the MCT layers. This is because as the CdTe layer thickness is reduced, more of the strain due to the large lattice mismatch is accommodated in the MCT layer.

The electron concentration for these layers, measured at 80 K, fell monotonically from $3.3 \times 10^{17}/cm^3$ to $1.2 \times 10^{16}/cm^3$ for increasing buffer layer thickness. This is to be expected, since strain-induced defects are known to act as n type in MCT[4]. A CdTe layer thickness of 2–3 μm was found necessary to fully accommodate the lattice mismatch

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THE ORGANOMETALLIC HETEROEPITAXY OF CdTe AND HgCdTe ON GaAs SUBSTRATES

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ABSTRACT

Heteroepitaxial films of CdTe and $Hg_{1-x}Cd_xTe$ have been grown on (100) GaAs substrates by organometallic vapor phase epitaxy. It is shown that high quality CdTe films can be grown on GaAs substrates over the temperature range from 350 ^oC - 440 ^oC. The effects of the reactant pressures on the growth rate of CdTe are also discussed. HgCdTe layers were grown, on GaAs substrates with a CdTe buffer layer, at 415 C. Transport measurements made on these layers indicate that they are of high quality with a 80 K mobility of over 2×10^5 cm^2/V-sec for layers of composition x 0.2. Layers have been grown with different buffer layer thicknesses. It is shown that a CdTe buffer layer of at least 2 - 3 microns is necessary to fully accommodate the misfit dislocation at the CdTe-GaAs interface.

1. INTRODUCTION

$Hg_{1-x}Cd_xTe$ (MCT) is an important intrinsic semiconductor material for infrared detector applications, especially in the 8-16 micron range. Epitaxial growth of this material on a suitable substrate has received considerable attention in the past few years. CdTe is a natural choice as a substrate material because of its excellent lattice match and chemical compatibility with MCT systems. However, the lack of availability of high quality, large area substrates of this material have prompted many workers to consider alternate substrates such as GaAs, InSb and sapphire. Of these, InSb, which is closely lattice matched to CdTe has been investigated by many workers.[1-4]

A disadvantage of using InSb as a substrate material is that it has a relatively low energy gap (0.22 eV at 77 K). This renders it optically opaque at wavelengths below 5 microns, so that it is an unsuitable substrate material for many backside illuminated photodetector applications. As a result, attention has focussed on the use of GaAs as an alternate substrate material because of its wider energy gap (E_g = 1.51 eV at 77 K). Moreover, its use opens up the possibility of integrating GaAs circuits with sensor devices of HgCdTe, in a monolithic structure.

The growth of CdTe and MCT on GaAs substrates by molecular beam epitaxy[5,6] (MBE) and organometallic vapor phase epitaxy[4,7,8,9] (OMVPE) has been the subject of study in recent papers. In addition, we have reported on the electron channeling patterns and photoluminescence properties of CdTe grown on GaAs[10] by OMVPE. Our work has shown that, although the lattice mismatch between CdTe and GaAs is over 14%, high quality single crystal layers with featureless morphology could be obtained over the 350-420 C range of growth temperatures. In this paper, we report

recent results obtained on the growth of CdTe on GaAs substrates and also on the growth and electrical characterization of MCT layers on GaAs substrates. These are grown by CMVPE, with an intermediate buffer layer of CdTe, in a continuous process. The effect of CdTe buffer layer thickness on the electrical properties of the MCT layer will also be discussed here.

2. EXPERIMENTAL

The epitaxial growth of CdTe and MCT was carried out in a system described previously.[11] Dimethylcadmium (DMCd) and diethyltelluride (DETe), held at $15^{\circ}C$, were used as the cadmium and tellurium sources respectively, and elemental mercury was used as the mercury source.

GaAs substrates, 7 mm x 7 mm in size and of (100) $2^{\circ} \rightarrow (110)$ orientation were cleaned in organic solvents and etched in Caro's etch (H_2SO_4: H_2O_2: H_2O = 5 : 1 : 1 by volume) for 10 minutes to remove 15-20 microns prior to epitaxial growth. After loading the substrates, the system was purged with nitrogen and brought up to the growth temperature in hydrogen.

First, a layer of CdTe was grown on GaAs; typically, partial pressures of $1 - 7 \times 10^{-4}$ atm were used for the DMCd, and $3 - 10 \times 10^{-4}$ atm for the DETe. Growth temperatures were in the range of $350 - 440^{\circ}C$. Specular surfaces of CdTe were obtained for these conditions. After the growth of the CdTe buffer layer, the MCT layer was grown at a substrate temperature of $415^{\circ}C$, without opening the reactor system. To do this, the reactor wall and the mercury chamber were first brought up to the required temperatures (230° C and $300^{\circ}C$ respectively). The susceptor was heated to 415 C in a DMCd ambient to prevent the decomposition of CdTe, and MCT growth was initiated by turning on the Hg and DETe flows.

3. RESULTS AND DISCUSSION

CDTe GROWTH:

Figure 1 shows a photograph of a 2.6 micron thick layer area sample. Typically, layers of this type were specular in character, with edge to edge flatness over the grown layer. The morphology of these layers is shown in Figure 2, under high magnification. Excellent layer morphology was observed over the full temperature range; however, the range of partial pressures of DMCd and DETe had to be optimized for each growth temperature. The achievement of good morphology became increasingly difficult at higher growth temperatures (440°C). We believe that this is due to the tendency of tellurium crystallites to form on the substrate at these temperatures. It is probable that three-dimensional growth, initiated by nucleation at these sites, leads to a deterioration in the morphology. An alternative possibility is the formation of a solid methylene polymer[12] at these temperatures, which would have the same consequence.

The growth rate of CdTe was studied at 350°C as a function of DMCd flow (with DeTe flow fixed) and also as a function of DETe flow (with DMCd flow fixed). The results are shown in Figure 3. A few observations can be made from these two figures. First, the growth rate is sublinear in both cases even when one of the reactants is a minority species. Next, for a fixed partial pressure of DETe, an increase of P_{DMCd} above 5×10^{-4} atm. does not have any effect on the growth rate. On the other hand, for a fixed partial pressure of DMCd, an increase of P_{DETe} above 5×10^{-4} atm. results in an increase in the growth rate, which eventually saturates at a higher value than for the previous case. Finally, we note that the growth is limited by surface kinetics at 350°C, even at low flow rates of DMCd or DETe.

The above results can be explained by assuming a Langmuir Hinshelwood model, where the deposition of CdTe occurs by the adsorption of these two reactants followed by a surface catalysed reaction.[13,14] From the second observation, we propose the following growth mechanism for CDTe: DMCd decomposes into (CH_3-Cd) or Cd at the surface and gets strongly chemisorbed. On the other hand, no such reaction occurs in the case of DETe. The eventual growth of CdTe occurs by the surface reaction of DETe and decomposition products of DMCd.

Growth rates at 440°C were considerably larger, because of the increased decomposition of DETe. Measurements in the sublinear region could not be made at this temperature, because of the resulting polycrystalline growth. Electron channeling studies, carried out on these layers, indicate that they are (100) oriented and of high crystal quality.[10]

Photoluminescence (PL) measurements were made on these layers at 77 K using a 7 mW He-Ne laser as the optical excitation source. Care was taken to use identical measurement conditions for all cases, so that this data is meaningful on a comparative basis. The PL spectra showed a bound exciton peak at 1.58 eV and a second peak at 1.43 eV which has been established to be due to the (Cd vacancy-donor) complex.[15] Figure 4 shows the ratio of the intensity of the defect peak to the bound exciton (I_{Cd}/I_{BE}) as a function of the P_{DMCd}/P_{DETe} ratio for a typical set of runs. A broad minimum is seen to occur for a P_{DMCd}/P_{DETe} ratio of unity. The existence of this broad minimum indicates that wide range of organometallic flow ratios can be used without deteriorating the electro-optical parameters of the grown layer.

HgCdTe GROWTH:

HgCdTe layers were subsequently grown at 415°C on these CdTe buffer layers. For all these runs, the buffer layers were grown at 350°C. Figure 5 shows the morphology of a MCT layer grown on GaAs. The layer is mirror-like to the unaided eye, but a small number of hillocks (about 500/sq. cm in number) are visible when viewed under the microscope. MCT layer grown on bulk CdTe substrates under ideal conditions do not result in such hillocks, indicating that they probably originate during the growth of CdTe buffer layers. The composition of these hillocks was checked by energy dispersive X-ray analysis and was found to be identical to the composition of the surrounding layer. It is well known that the growth rate of HgTe increases near defects or sample edges because these provide easy nucleating sites. Hence, any defect or kink site on the CdTe epilayer will probably result in a hillock in the MCT layer. Such defects can be expected to occur, in the form of stacking faults,[16] because of the large lattice mismatch between CdTe and GaAs.

Hall and resistivity measurements were made from 10 to 300 K by means of the Van der Pauw method, patterned in the form of a cloverleaf, with a magnetic field strength of 2.1 kG. Indium solder was used for the contacts in all these measurements. Figure 6 shows the Hall mobility versus temperature data for a MCT layer of composition $x \simeq 0.2$. This layer was grown with a CdTe buffer layer thickness of 2.6 microns, and had a MCT layer thickness of 5.6 microns. The maximum value of the mobility for this layer is 2.1×10^5 cm^2/V sec at 80 K.

Figure 7 shows the Hall coefficient (R_H) as a function of inverse temperature for the layer shown in Figure 6. From the value of R_H at low temperature ($\simeq 10$ K), the carrier concentration in this layer is estimated to be approximately 2.3×10^{15} cm^{-3}.

The effect of the buffer layer thickness on the properties of the MCT layers was also studied. Figure 8 presents the electron mobility at 80 K, for a number of MCT layers with x in the 0.18 to 0.21 range. All layers were grown under identical conditions except that the thickness of the CcTe film was varied. The composition variation x over a 5 mm x 5 mm region was approximately 0.01. We note that the thickness of the buffer layer has a strong effect on the electron mobility in the MCT layers. This is because, as the CdTe layer thickness is reduced, more of the strain due to the large lattice mismatch is accommodated in the MCT layer.

The electron concentration for these layers, measured at 77 K, fell monotonically from $3.3 \times 10^{17}/cm^3$ to $1.2 \times 10^{16}/cm^3$ for increasing buffer layer thickness. One possible cause for this behavior is the doping of MCT layers by gallium diffusion from the substrate through the CdTe buffer layer. However, the electrical properties of our CdTe buffer layers have shown that they are semi-insulating. Hence, doping from the GaAs substrate can be discounted as the reason for this relatively high doping. We believe that the electron concentration in MCT layers with a thin CdTe buffer results from strain, since strain induced defects are known to act as n-type in MCT.[17]

A CdTe layer thickness of 2-3 microns was found necessary to fully accommodate the lattice mismatch between GaAs and CdTe systems, and give layers with a large value of Hall mobility, and low carrier concentration. Transmission electron microscopy (TEM) studies done on CdTe layers grown on GaAs by other workers[16,18] have shown that the density of dislocations near the CdTe/GaAs interface is approximately $10^{11}/cm^2$. At distances exceeding 2-3 microns, the dislocation density was reduced to

$10^5/cm^2$ suggesting that the misfit stress between CdTe and GaAs is effectively accommodated over this distance. Our study also supports the above view from the measurements of the transport properties.

4. CONCLUSION

The OMVPE growth of MCT layers, grown on GaAs substrates, with an intermediate buffer layer of CdTe, was demonstrated. Except for the presence of a few hillocks, the morphology of the layers are featureless. More studies need to be done to determine the cause of these hillocks, and for their reduction. The transport properties of these layers were reported, and their high quality established by this data. These electrical measurements indicate that the misfit stress between GaAs and CdTe is accommodated between 2-3 microns from the CdTe/GaAs interface. However, a detailed study will be required to confirm this point.

FIGURES

Figure 1: A 2-6 micron thick CdTe layer on GaAs. The reflection of the 1 mm scale markers demonstrates its specular character.

Figure 2: Morphology of CdTe layers grown on (100) GaAs misoriented $2^{\circ} \rightarrow$ (110).

Figure 3: Growth rate as a function of (a) P_{DETe} with P_{DMCd} = 5 × 10^{-4} ($\triangle$); (b) P_{DMCd} with P_{DETe} = 5 × 10^{-4} atm (0).

Figure 4: The ratio of the intensity of the Cd vacancy-donor complex defect peak to the boundary exciton peak, plotted as a function of P_{DMCd}/P_{DETe}.

Figure 5: Morphology of $Hg_{1-x}Cd_xTe$ layer grown on (100) GaAs. The thickness of the CdTe buffer layer is 0.2 microns and composition $x \simeq 0.2$.

Figure 6: Electron mobility in HgCdTe ($x \simeq 0.2$) as a function of temperature. The layer was grown with 2.6 micron thick CdTe buffer layer.

Figure 7: Hall coefficient versus reciprocal temperature for the layer of Figure 6.

Figure 8: Electron mobility in HgCdTe layers, as a function of the CdTe buffer layer thickness. The composition x is shown in parenthesis.

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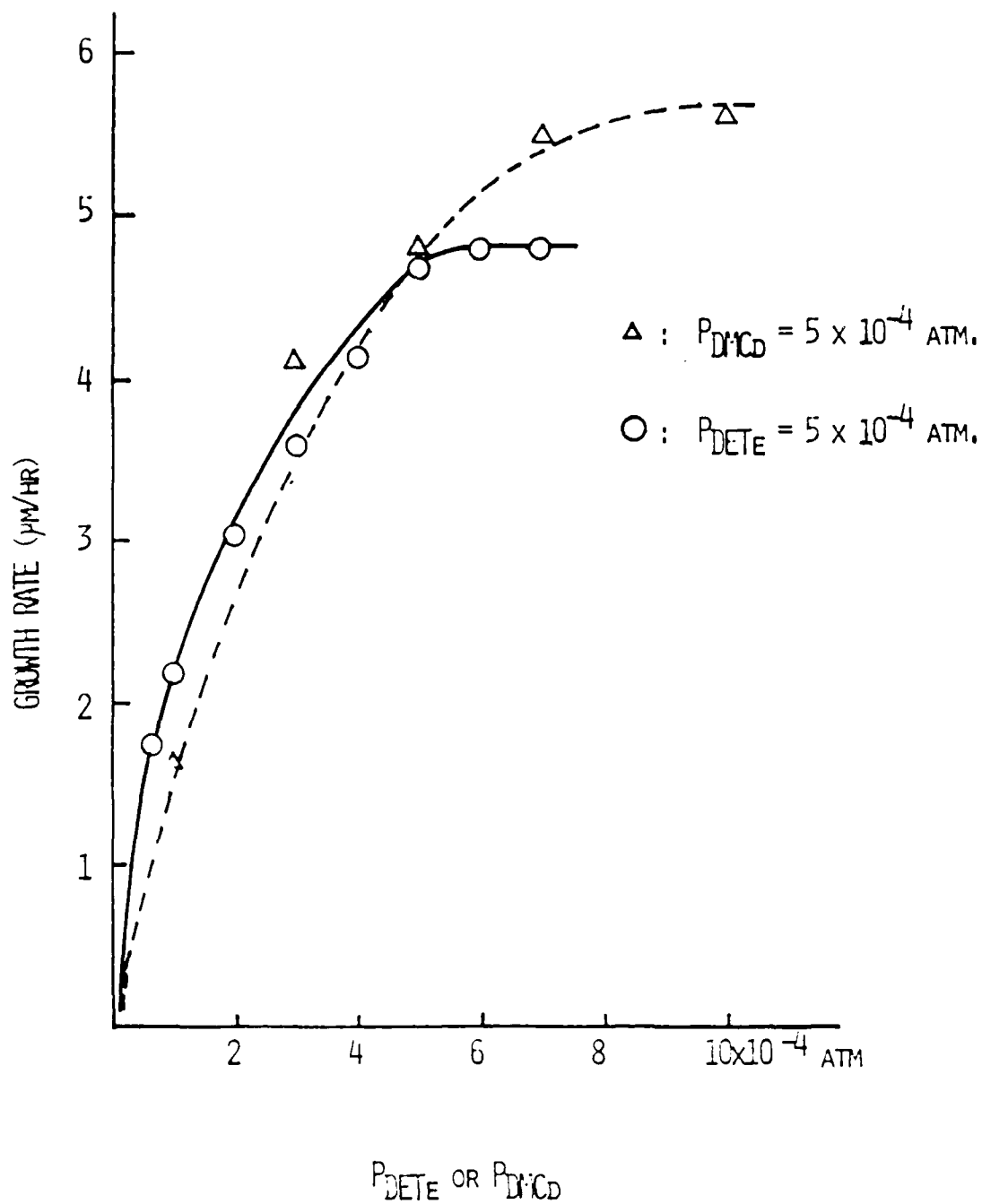18.   J. T. Cheung, M. Khoshnevisan and T. Magee, Appl. Phys. Lett. 43, 462 (1983).
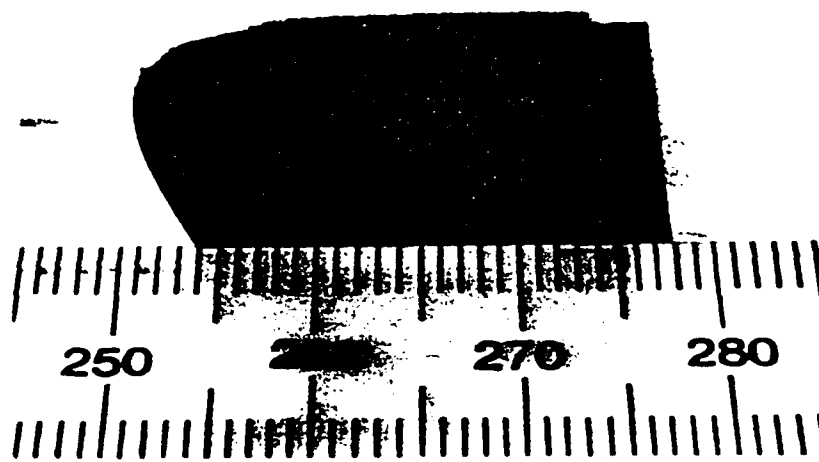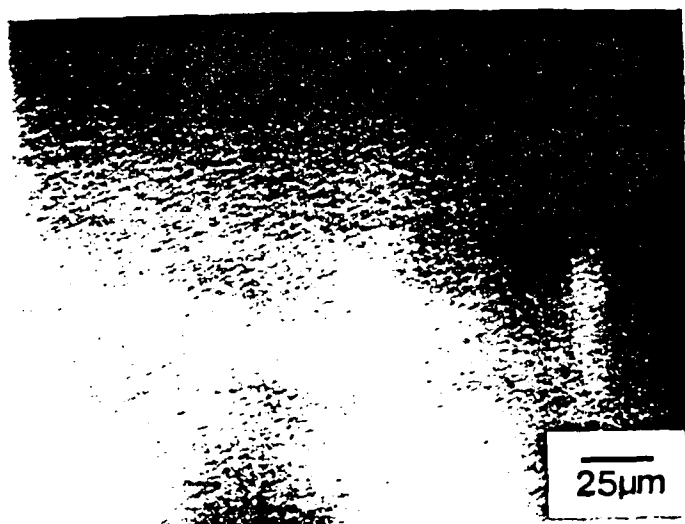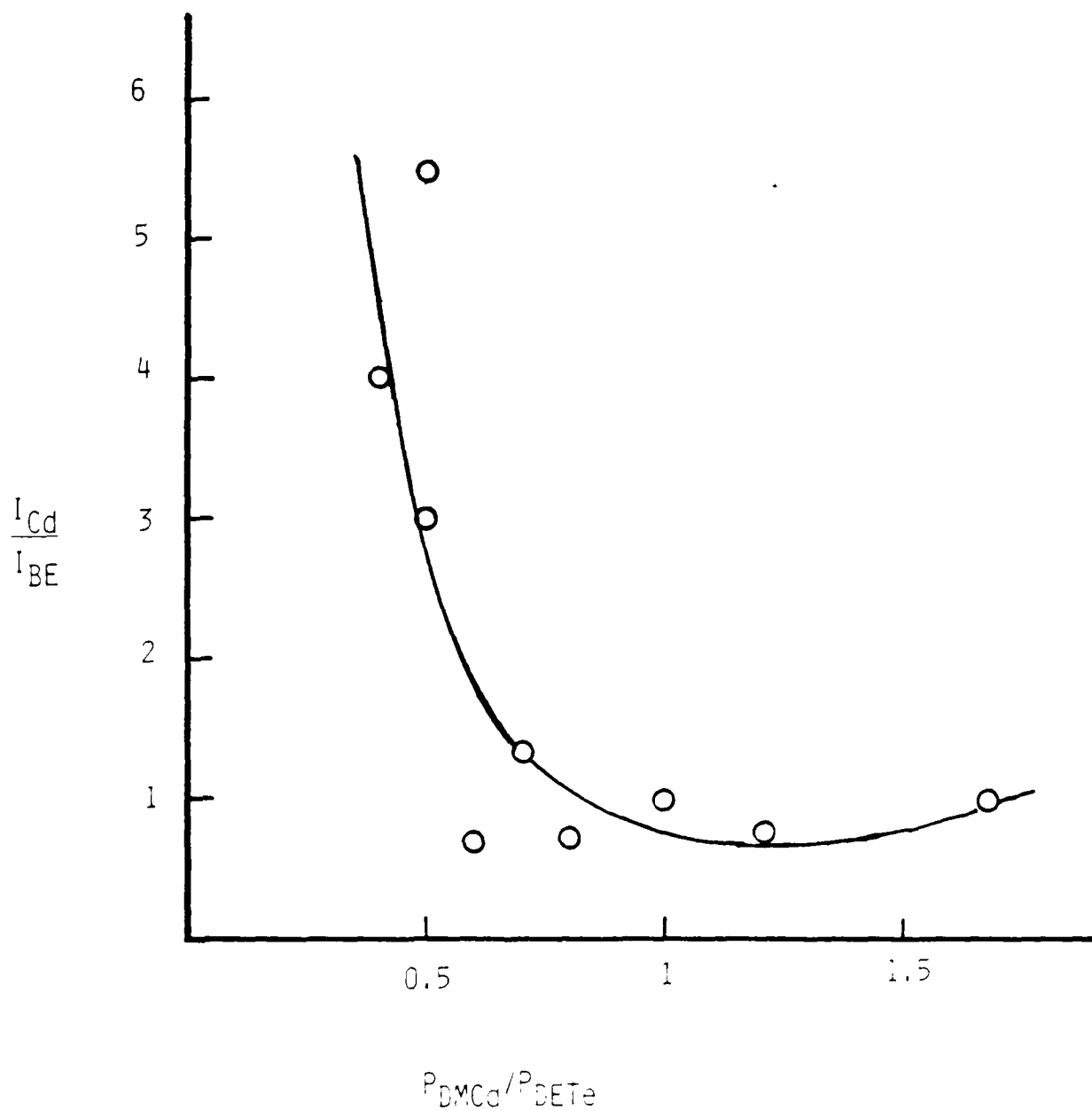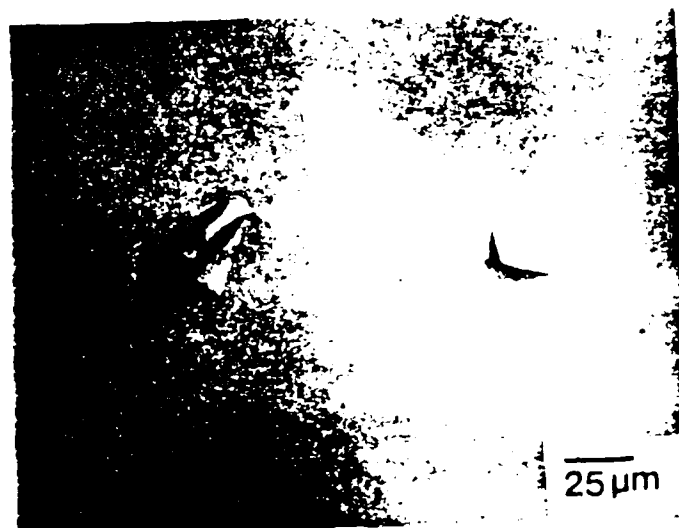
250   2~~~   270   280

FIG-1

I Bhat et al

25µm

FIG 2

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FIG 3

FIG 4

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25 μm

FIG 5

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FIG 6

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FIG 7

Electron Mobility, μ (cm^2/V-sec)

4×10^5

2×10^5

10^5

10^4

(0.18)

(0.19)

(0.205)
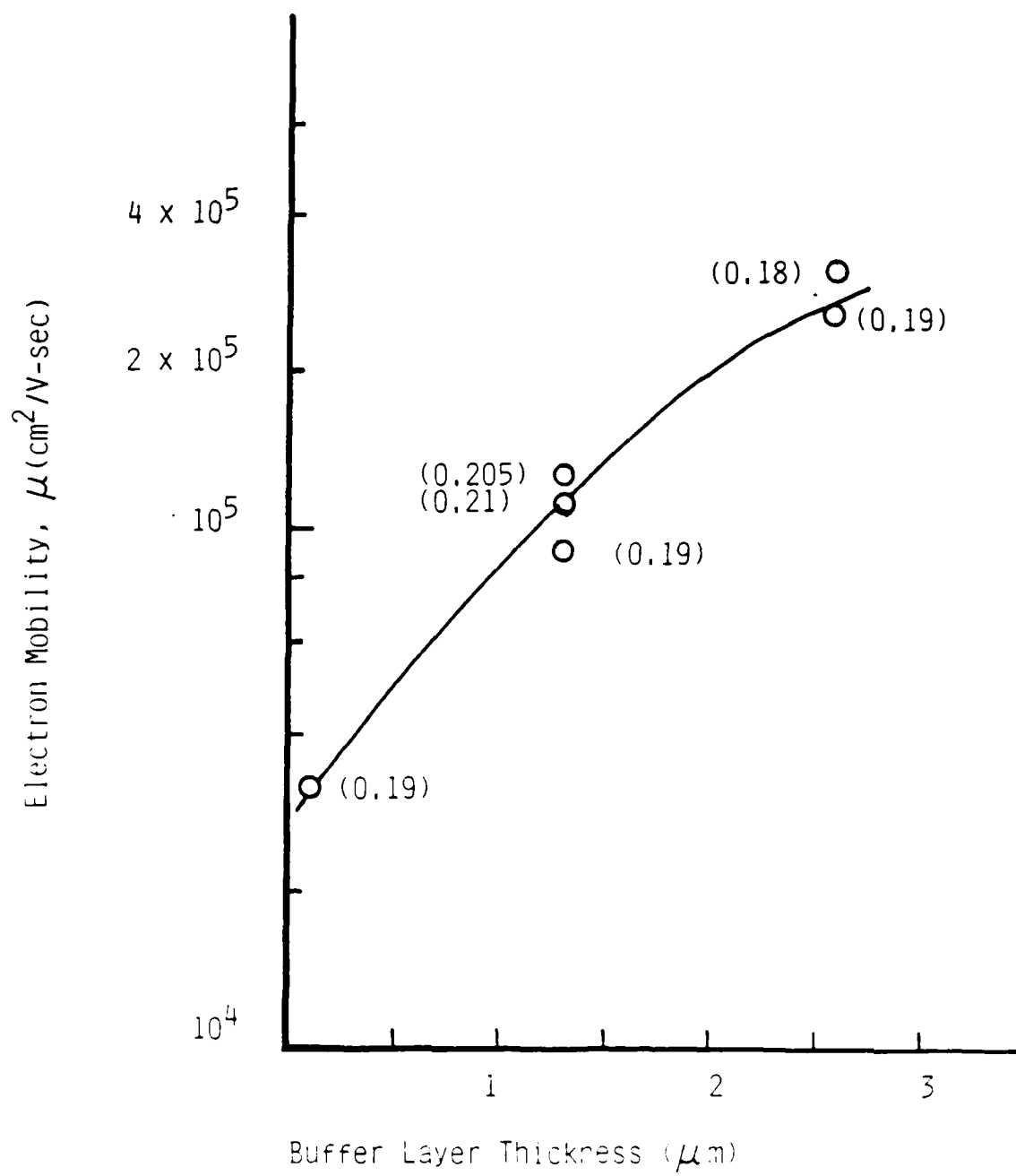(0.21)

(0.19)

(0.19)

1

2

3

Buffer Layer Thickness (μm)
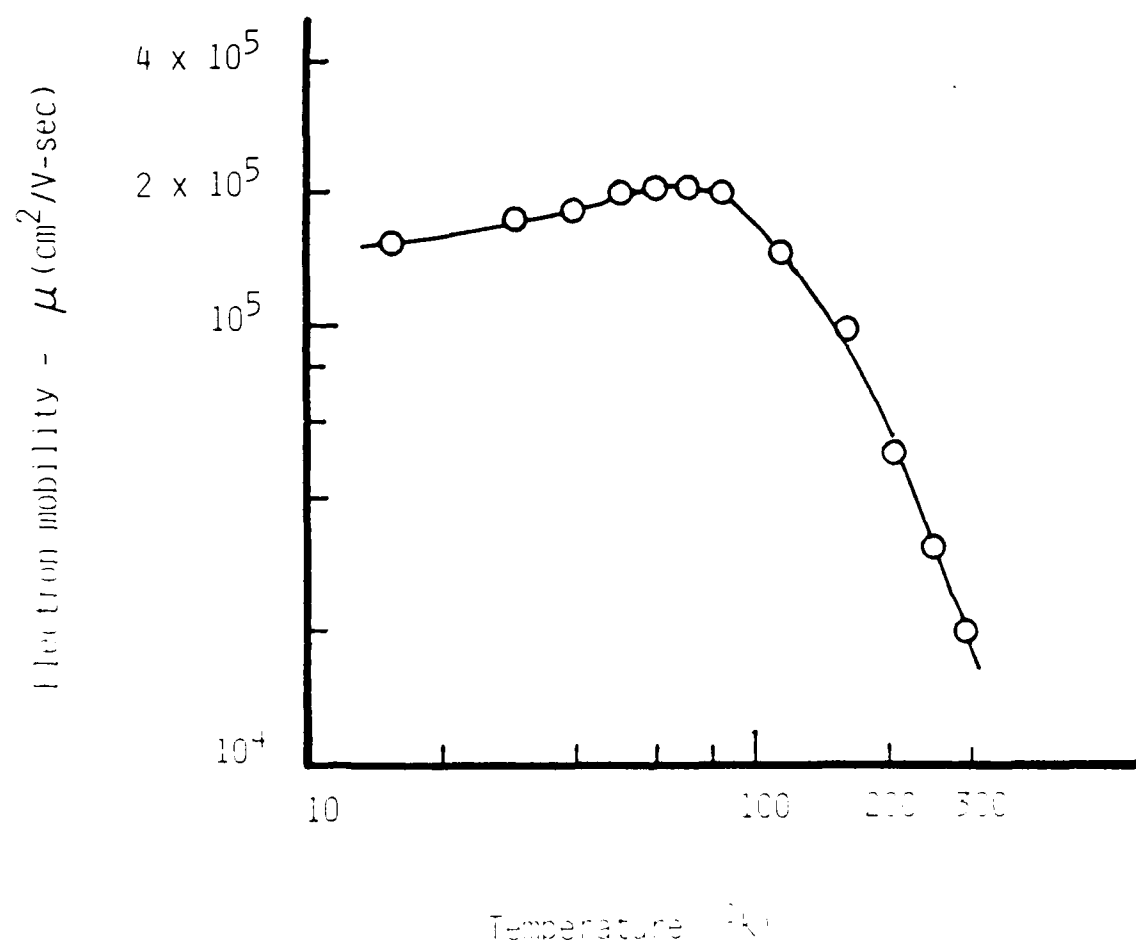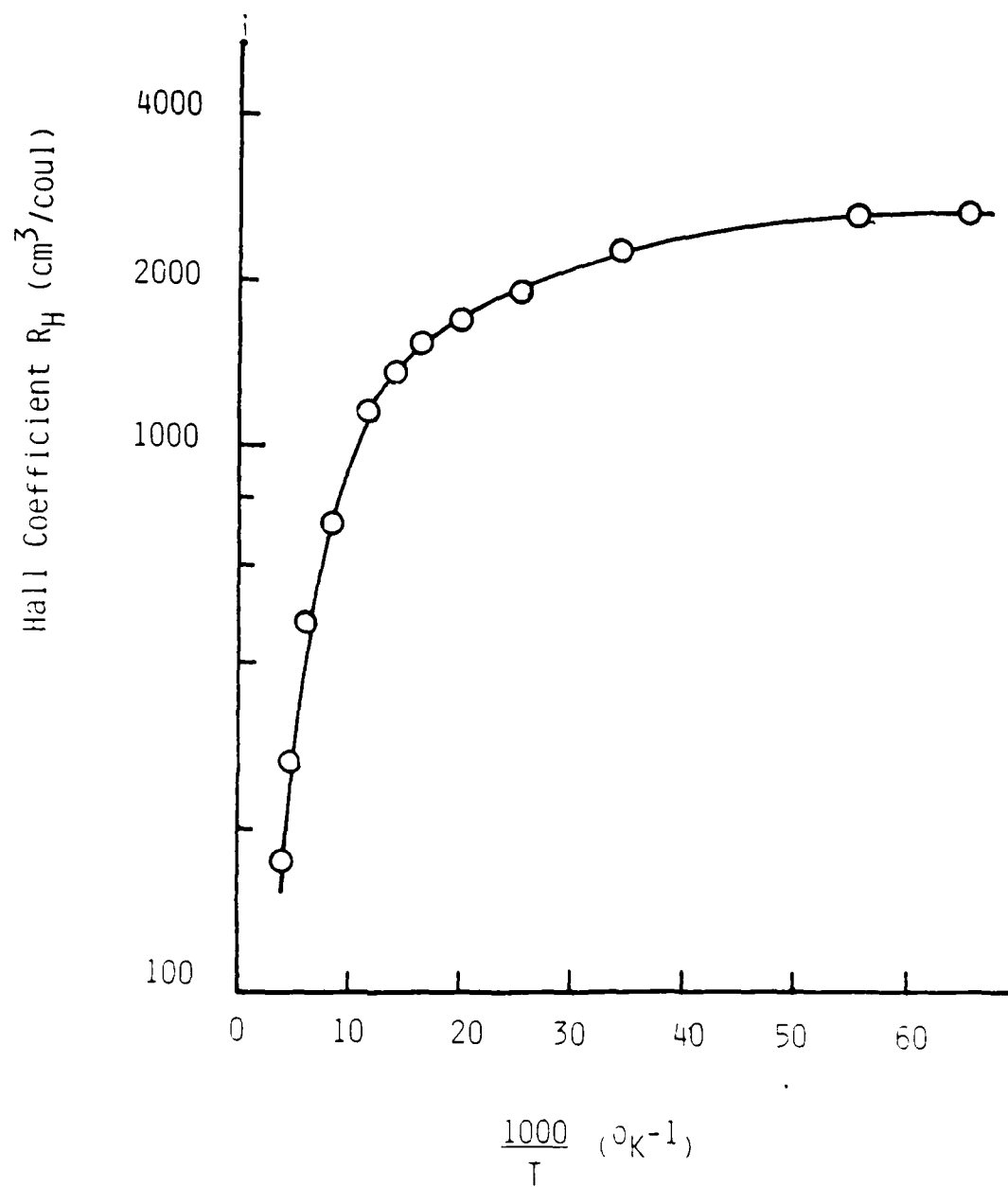
Bhat et al

FIG 8

THE GROWTH OF MERCURY CADMIUM TELLURIDE BY ORGANOMETALLIC EPITAXY

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ABSTRACT

$Hg_{1-x}Cd_xTe$ layers have been grown on CdTe substrates using dimethyl-cadmium, diethlytelluride and mercury in a horizontal reactor. Details of conditions for growth of these layers is provided in this paper. Specular surfaces of $Hg_{1-x}Cd_xTe$ with $x \geq 0.15$ were obtained on (100) $3° \rightarrow$ (110) oriented CdTe substrates. The morphology of the layers with various compositions is also presented here. Both n-type and p-type layers could be obtained The mobility of these layers was measured over the temperature range of 10 K to 300 K. The mobility of n-type of $Hg_{.81}Cd_{.19}Te$ layers, measured at 2.1 kGauss, was 3.0×10^5 cm^2/V-sec at 60 K, falling to 2×10^5 cm^2/V-sec at 10 K. P-type layers were also grown, and are described in this paper. Anomalous behavior was observed in some of these p-type layers. Reasons for this behavior are presented in this paper.

Introduction

The epitaxial growth of $Hg_{1-x}Cd_xTe$ has received considerable attention during the past several years, because it potentially can yield active layers of better electrical quality than those grown by bulk methods. Moreover, active thin layers are required in a number of integrated circuit type applications using this material. Several methods have been reported for the growth of these layers; among them, organometallic vapor phase epitaxy (OMVPE) is a very promising candidate.

The growth of $Hg_{1-x}Cd_xTe$ by OMVPE was reported by several workers (1-5) but no detailed experimental conditions such as the reactant partial pressures are available. Our own work on the growth of this material, and on the results of electrolyte electroreflectance measurements taken on these layers, was reported in two communications (6,7).

In this paper, we report on the details of growth of HgCdTe, and on electrical characteristics of both p- and n-type layers. The work represents an extension of our work on the growth of HgTe by OMVPE (8).

Experimental

Epitaxial growth of HgCdTe was carried out at atmospheric pressure in a quartz horizontal reactor tube, using palladium purified hydrogen as the carrier gas. Diethyltelluride (DETe) and Dimethylcadmium (DMCd)[1] vapors were used as organometallic sources of Te and Cd respectively, and were introduced by bubbling hydrogen through the respective bubblers which were

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1. Alfa-Ventron, Danvers, Massachusetts 01923

held at 15°C. The mercury source was provided by passing hydrogen over mercury which was held at 300°C.

The main reactor tube was 51 mm diameter and used a 25 × 25 × 60 mm RF-heated graphite susceptor placed 6 cm from the inlet. Susceptor temperature was monitored by means of a quartz-sheathed Type K thermocouple in a 6.5 mm hole in the rear of the susceptor. The tube wall in front of the susceptor was heated to prevent mercury condensation. A temperature of 200 - 250°C was used for this purpose.

Substrates used for epitaxial deposition were (100) CdTe wafers[2] 4 mm × 4 mm in size, misoriented 3° towards the (110) direction, and polished on one face. These were first cleaned in organic solvents, after which about 20 microns was etched off in a 2% Br-methanol solution to result in highly polished surfaces.

Growth runs were made at substrate temperatures from 400 - 430°C, with the hydrogen set to 1 ℓ/min. Once growth was terminated, the total hydrogen flow was increased to 3.2 ℓ/min to facilitate a faster cool down. The hydrogen flow was maintained until the susceptor reached 150°C, from which point onwards nitrogen gas was used to purge the system. The samples were removed from the system when the susceptor temperature fell below 100° C.

The thickness of the deposited layer was measured gravimetrically. Both the composition-dependent specific gravity, as well as growth on sample edges, were taken into account for this computation. In some cases,

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[2] Two-Six Incorporated, Saxonburg, Pennsylvania 16056

thickness was verified by scribing the substrates and then observing with the aid of a scanning electron microscope. No separate etching was necessary to delineate the interface.

The composition of the deposited layers was determined by from a plot of α^2 vs photon energy. A Perkin-Elmer Model 298 double-beam spectrophotometer with a CdTe wafer in the reference beam was used for this purpose. Layer thicknesses were in the 3-5 μm range. Electrical measurements were made by the van der Pauw technique, on a clover leaf pattern which was delineated in the epitaxial layer. Ohmic contacts were made to these layers by means of indium solder.

Results and Discussion

Initial runs were made over a wide range of reactor conditions in order to establish the conditions for the growth of good epitaxial layers. From these, it was found that the composition of the epitaxial layer was primarily determined by the DMCd flux in the gas phase, and secondarily by the partial pressures of DETe and mercury, for the growth of $Hg_{.8}Cd_{.2}Te$. Material with this composition was obtained at 415°C when the partial pressure of mercury was 0.04 atms, the partial pressure of DETe was 2.5×10^{-3} atms and the partial pressure of DMCd was 5×10^{-5} atms. A total hydrogen flow of 1 ℓ/min was used in conjunction with these growth conditions. The wall temperature was generally kept at around 230°C; this temperature was chosen to prevent mercury condensation on the wall in front of the susceptor.

<u>Layer Morphology</u>: CdTe substrates with (100) and (100) $3° \rightarrow$ (110) orientation were used to investigate the optimum orientation for the growth of HgCdTe. Mirror shiny layers could be obtained on all (100) $3° \rightarrow$ (110) oriented CdTe substrates, for $Hg_{1-x}Cd_xTe$ layer with $0.15 \leq x \leq 0.5$. Growth on (100) oriented substrates resulted in non-specular layers with a high density of hillocks. Consequently, all further work was confined to misoriented substrates.

The composition of the layer was found to have strong influence on the growth morphology. This is illustrated in Fig. 1 where the morphology of HgCdTe layers of different compositions are shown. Figure 1(a) shows the layer morphology of HgTe, which reveals large irregular steps with a very rough, hazy looking surface. A small addition of CdTe dramatically improves the surface morphology, as seen in Fig. 1(b). Here, $Hg_{1-x}Cd_xTe$ with a composition $x = 0.06$ had steps which are much closer together but are still clearly visible. As the CdTe fraction in the layer is increased further, (beyond $x \geq 0.15$), these steps are mostly annihilated resulting in specular surfaces, as shown in Fig. 1(c). The reason for this rapid improvement in surface morphology can be explained as follows (1). In the absence of Cd, once a nucleating site is formed, further nucleation in the vicinity of this site is unlikely due to the weak bond strength between Hg and Te ($\cong 13$ kcal/mole). Any adsorbed mercury will probably diffuse along the surface until it reaches a growth step. The presence of Cd will increase the density of nucleating sites because of the stronger bond strength between Cd and Te ($\cong 23$ kcal/mole). Hence, the nucleating sites will coalesce together to result in smooth surface morphology.

<u>Growth Rate and Composition</u>: The susceptor temperature had a strong influence on the growth rate and composition of the layers, as shown in Fig. 2 and Fig. 3 respectively. This behavior can be explained by noting that the growth rate of HgTe increases rapidly as the susceptor temperature is increased, due to increased DETe decomposition (8,9). On the other hand, the growth of CdTe is relatively constant above 400°C (10). Hence, the increase in the growth rate in Fig. 2 is largely due to an increase in the deposition of HgTe at higher temperature. This will cause a reduction in the composition x of the layer with temperature as seen in Fig. 3. Excellent control of the susceptor temperature was found to be critical in obtaining uniformity in composition, both across the wafer and as a function of the layer thickness. The composition variation x across the wafer was determined using energy dispersion X-ray analysis and was found to be x = 0.01.

<u>Mobility and Hall Coefficient</u>: The variation in the Hall mobility was examined over a temperature range of 10 K to 300 K and for a magnetic field strength of 2.1 kG for $Hg_{1-x}Cd_xTe$ samples with $x \leq 0.3$. Good ohmic behavior over the full temperature range was achieved by the use of indium contacts for this range of composition.

The effects of temperature on the mobility for three n-type samples are shown in Fig. 4. These samples were obtained by keeping the mercury partial pressure unchanged during cool down to 100°C. These results are representative of extrinsic n-type samples. Since the electron mobility is much higher than the hole mobility for these layers, the values given at all temperatures can be taken as the electron mobility, even though the material is intrinsic at higher temperatures. The rapid fall of the electron mobility at temperatures above approximately 100 K results from the

dominance of lattice scattering mechanisms. The slight fall in electron
mobility at low temperature   (10-50 K) can best be explained by taking
ionized impurity scattering effects into account (11). The effects of these
two scattering mechanisms result in a maximum in the mobility characteristic
at around 60 K. The mobility of these samples fell by only about 7% when
the applied magnetic field was increased from 2.1 KG to 4.5 KG, thus con-
firming that the material is truly extrinsic.

The Hall coefficient R_H versus temperature for these three samples is
plotted in Fig. 5. This coefficient is negative at low temperatures
(because an excess of donors dominate extrinsic conduction), and remains
negative in the intrinsic range at higher temperatures (because the electron
mobility is greater than the hole mobility).

No carrier freeze-out into discrete impurity levels was observed even
up to 10 K. This behavior is consistent with the very low effective mass of
conduction band electrons; as a consequence the donor level is merged into
the conduction band so that the electron concentration remains constant at
all temperatures (12). Extrinsic electron concentrations were calculated
from the low temperature Hall coefficient assuming $n_c = (q R_H)^{-1}$, and were
in the range $1 - 5 \times 10^{15}$ cm^{-3}.

The effect of composition on the Hall coefficient is also seen from
the three curves of Fig 5. For the sample with composition $x = 0.19$, the
Hall coefficient shows intrinsic behavior over a wide temperature range
above 50 K whereas for samples with $x = 0.25$, the intrinsic region in the
Hall coefficient is present above approximately 100 K. Below 100 K, the R_H
shows extrinsic behavior and has a constant value of 6600 cm^3/C. For

samples with composition x below 0.17, which have zero or negative bandgap, no extrinsic region in the Hall coefficient is observed and the R_H value will continue to increase down to the lowest temperatures. For the example shown with x = 0.16, extrinsic behavior is not observed, even at 13 K.

P-type layers were obtained when the samples were removed from the reactor, into air, upon reaching 350°C. If residual impurities are not dominant, this should result in p-type layers, as obtained here [13]. The hole mobility and Hall coefficient versus temperature curves for two p-type $Hg_{0.8}Cd_{0.2}Te$ samples are shown in Figs. 6 and 7 respectively. Sample A shows normal p-type behavior. Here, the Hall coefficient is negative at higher temperatures because the material is intrinsic and the electron mobility is higher than the hole mobility. The change over from negative to positive Hall coefficient takes place at about 50 K. The hole mobility is about 600 cm^2/V-sec at 15 K which is the typical value reported for lightly doped $Hg_{0.8}Cd_{0.2}Te$ samples (14). The p-type carrier concentration is about 1×10^{16} cm^{-3} which is obtained from the Hall coefficient at low temperature. No clear extrinsic region in the Hall coefficient is seen, probably because the extrinsic region and the region at which R_H reverses sign overlap.

The situation is somewhat different, however, for sample B which shows anomalous behavior. Here, the Hall coefficient does not reverse sign at low temperature, but remains negative and low. A rapid rise in the resistivity is often observed in samples of this type at low temperature. One explanation for this behavior , at least qualitatively, is that a surface oxide is produced during the cool down phase, resulting in an n-type surface inversion layer on the p-type epitaxial film (15,16). This can

effectively isolate the bulk of the film from the external Hall and resistivity probes at low temperature. Hence, low temperature electrical measurements will give the mobility and carrier concentration of this inversion layer rather than the electrical properties of the p-type epitaxial film.

An alternate possibility is that the epitaxial film is graded in carrier concentration, being n-type at the surface and increasingly p-type with depth. This may come about because the sample is cooled down to 350° C in a mercury rich ambient, resulting in an n-type surface, whereas the bulk of the layer may remain p-type because of the presence of mercury vacancies. This could cause a n-p junction to form at low temperature and result in the electrical characteristic described here.

Electrical anomalies of this type have been reported for HgCdTe samples having hole concentration less than 2×10^{17} cm^{-3}. Another type of anomaly encountered in HgCdTe is the double crossover (17) where the Hall coefficient changes sign twice, going from negative to positive and back to negative as the temperature is reduced from 300 K to 4K.

Conclusions

$Hg_{1-x}Cd_xTe$ layers have been grown on misoriented (100) CdTe substrates by OMVPE using elemental mercury, DETe and DMCd. Their characteristics have been studied at different growth temperatures. The morphology of the layers with various composition was presented. It was found that specular surfaces could be obtained for layers with composition x 0.15. The electrical characteristics of the layers were studied over the temperature range 10 K to 300 K. Measurements of these layers show that

their properties are comparable to the best bulk and epitaxial [2] material which can be obtained today.

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FIGURES

Figure 1: Optical micrographs of $Hg_{1-x}Cd_xTe$ epitaxial layers of three different compositions (a) $x = 0$ (b) $x = 0.06$ (c) $x = 0.2$. The markers are 25 m long.

Figure 2: Growth rate of $Hg_{1-x}Cd_xTe$ layer versus susceptor temperature. $P_{Hg} = 0.04$ atm, $p_{DMCd} = 4 \times 10^{-5}$ atm, $p_{DETe} = 2.5 \times 10^{-3}$ atm and total flow = 1 ℓ/min.

Figure 3: Variation in the composition x as a function of the susceptor temperature, for the same reactor conditions as shown in Figure 2.

Figure 4: Variation of Hall mobility with temperature for three n-type $Hg_{1-x}Cd_xTe$ layers.

Figure 5: The variation of Hall-coefficient R_H with reciprocal temperature for the samples of Figure 4.

Figure 6: the Hall mobility as a function of temperature for two p-type $Hg_{1-x}Cd_xTe$ layers. Nominal composition $x = 0.2$.

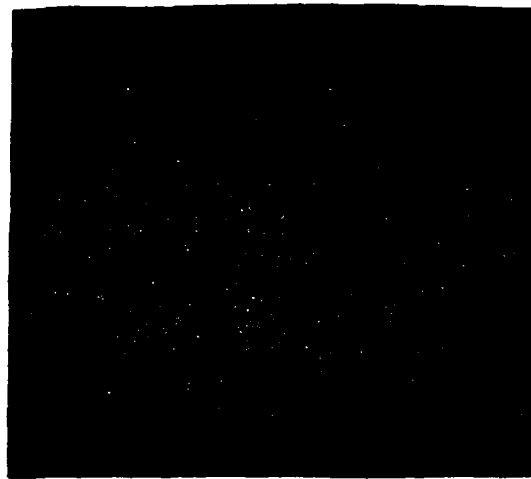Figure 7: The Hall-coefficient R_H as a function of reciprocal temperatures for the samples of Figure 6.
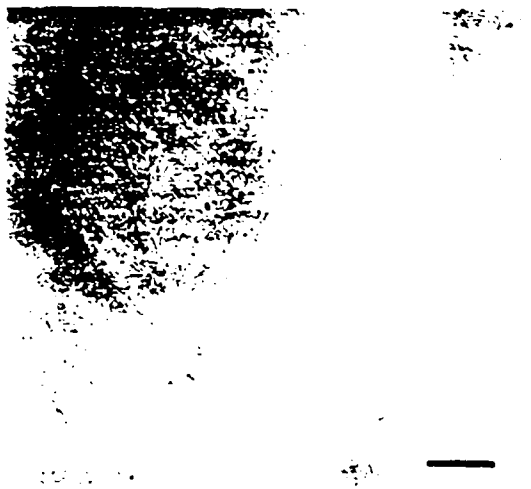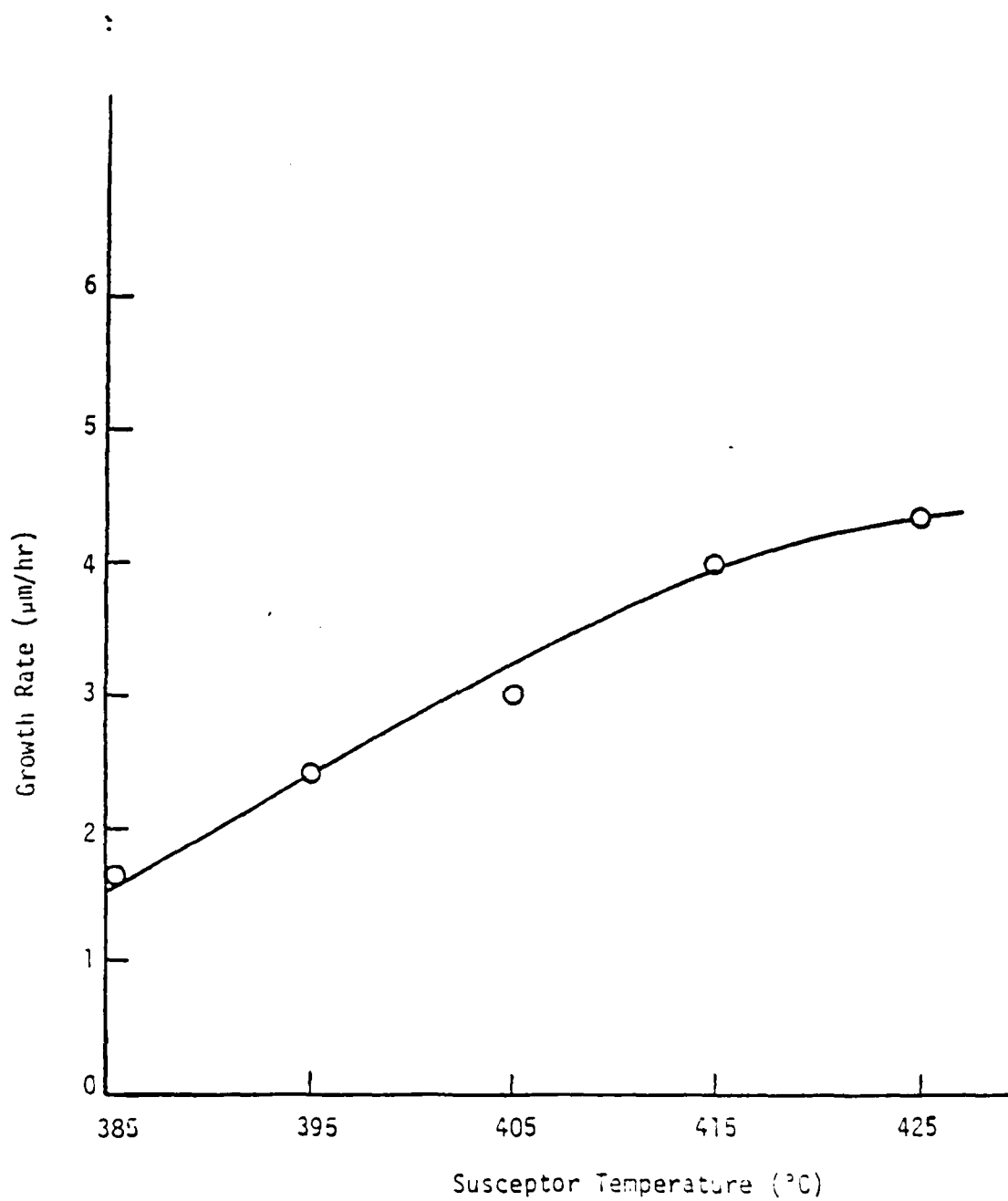
FIG 1

FIG 2

FIG 3
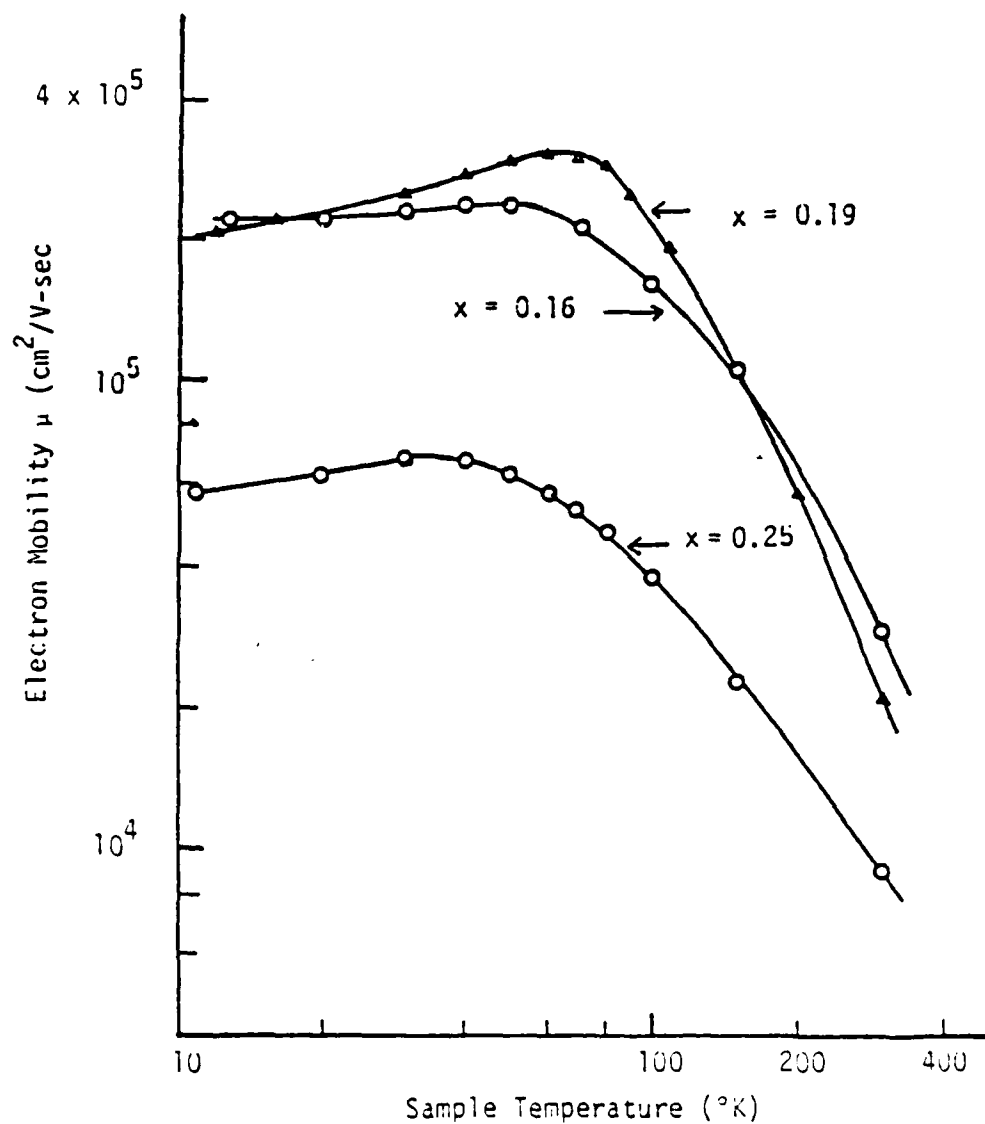
FIG 4

FIG 5
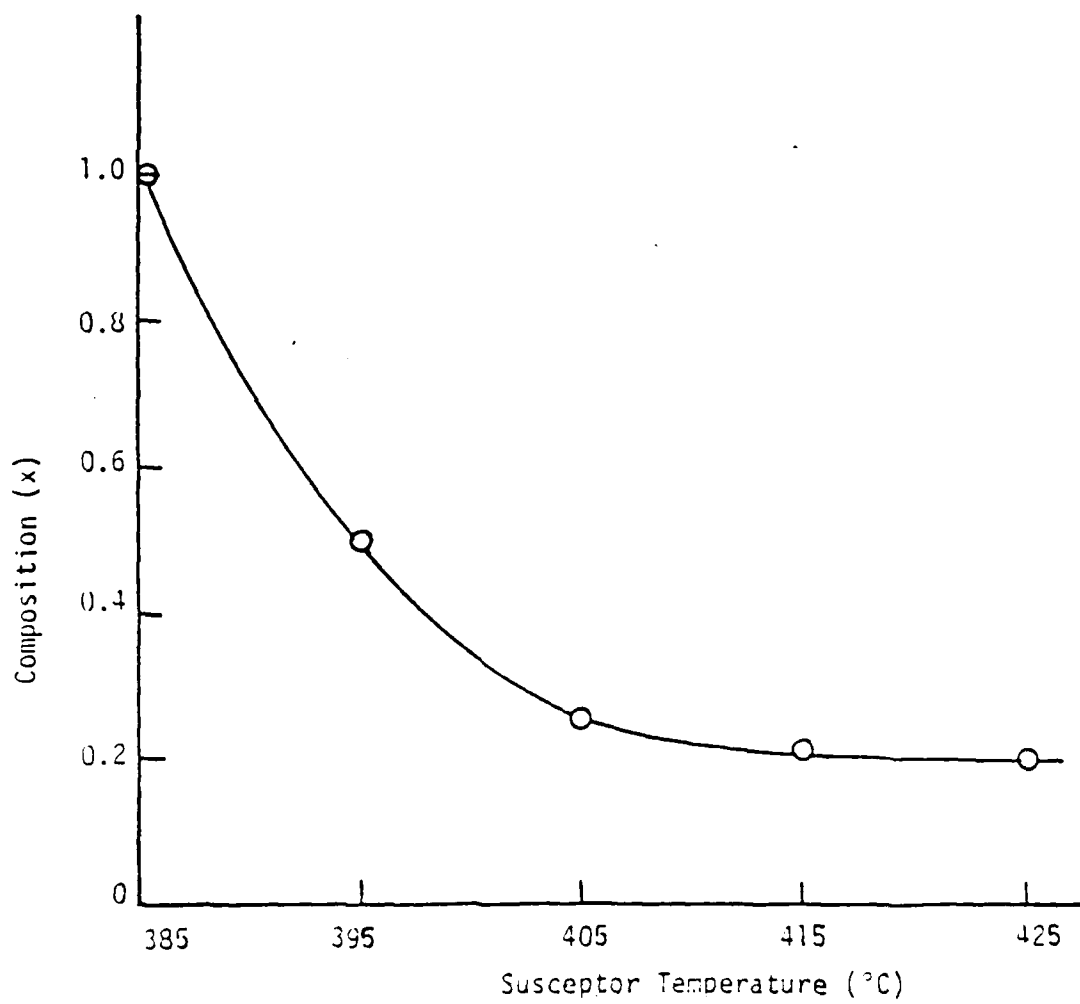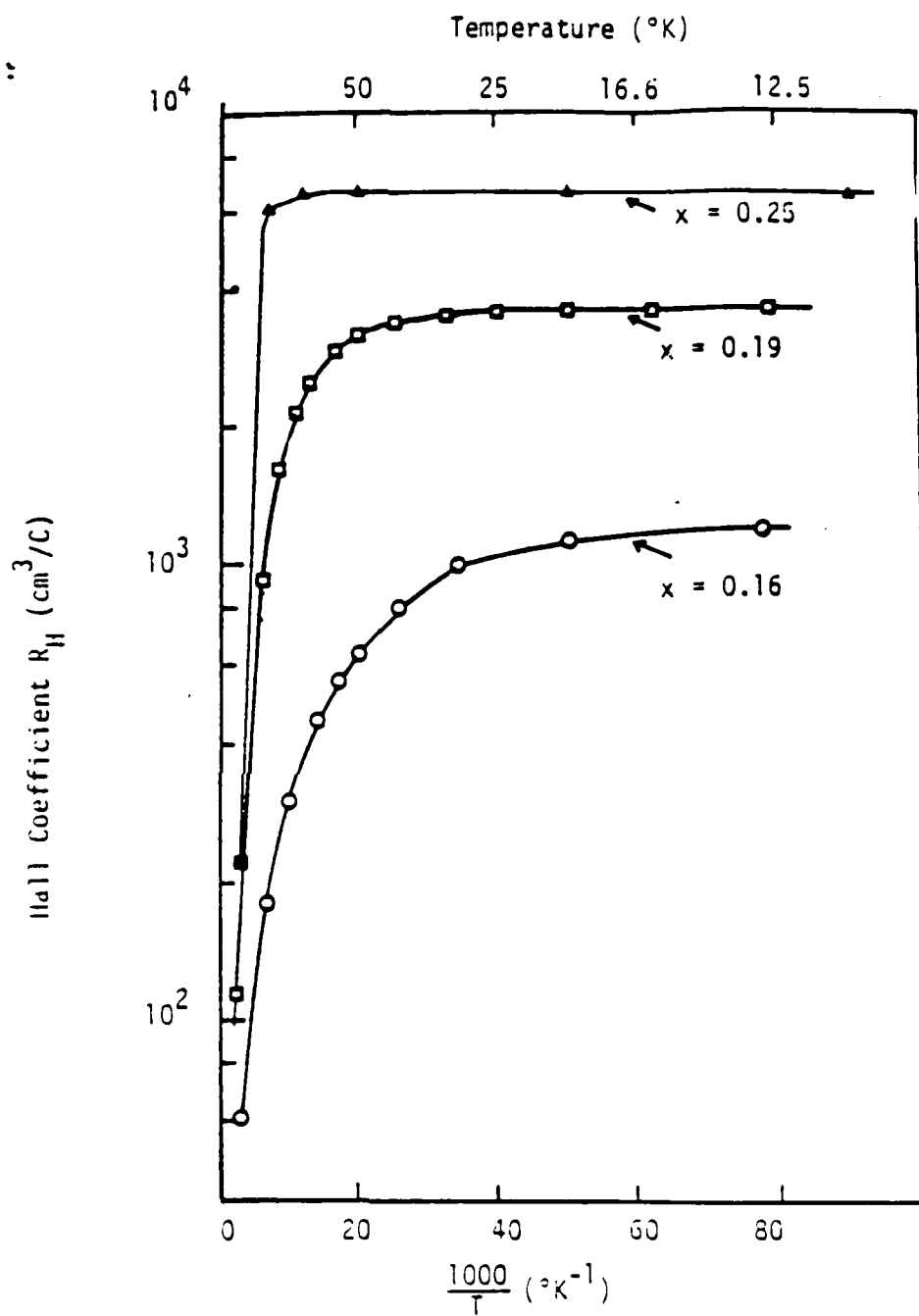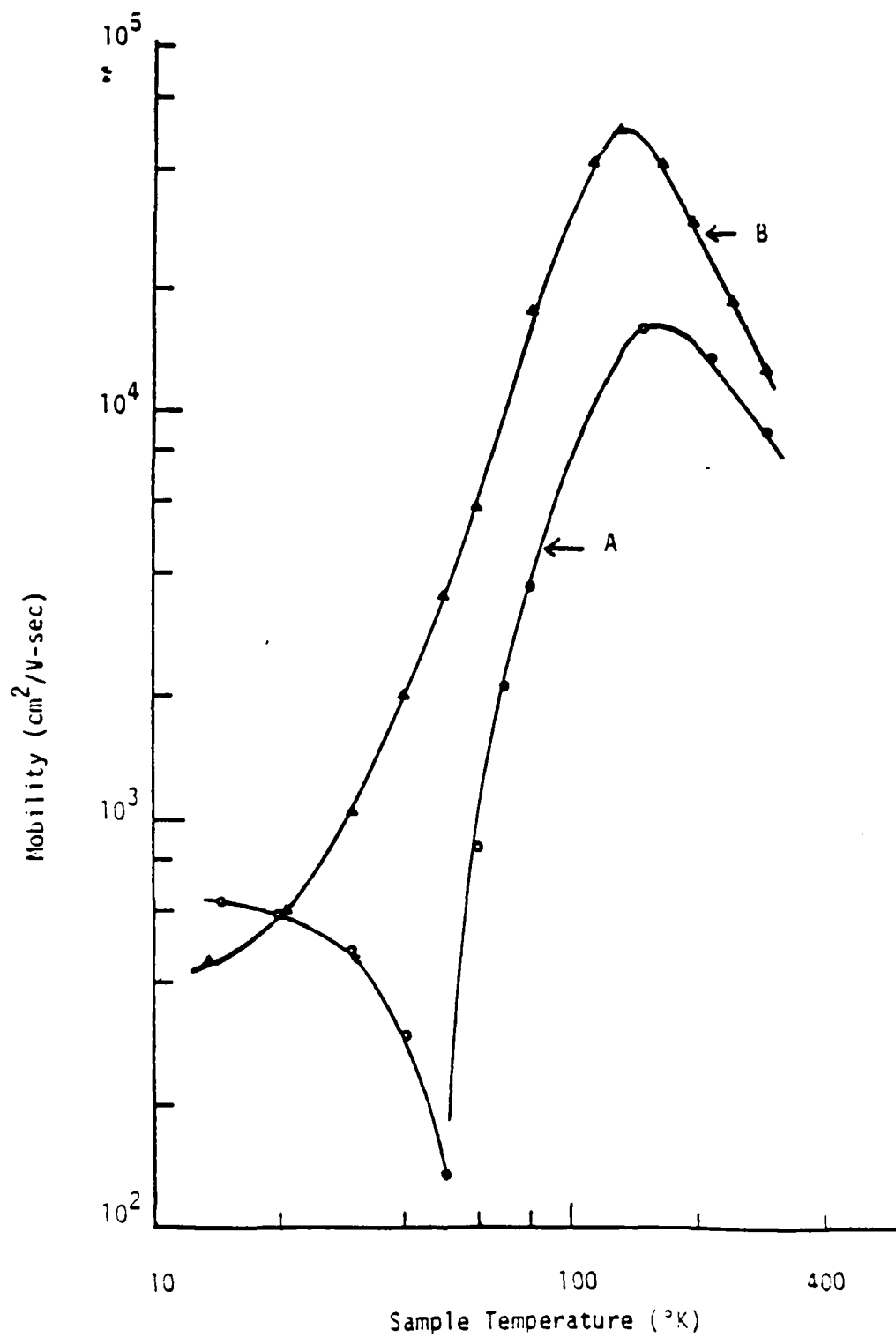
FIG # 6
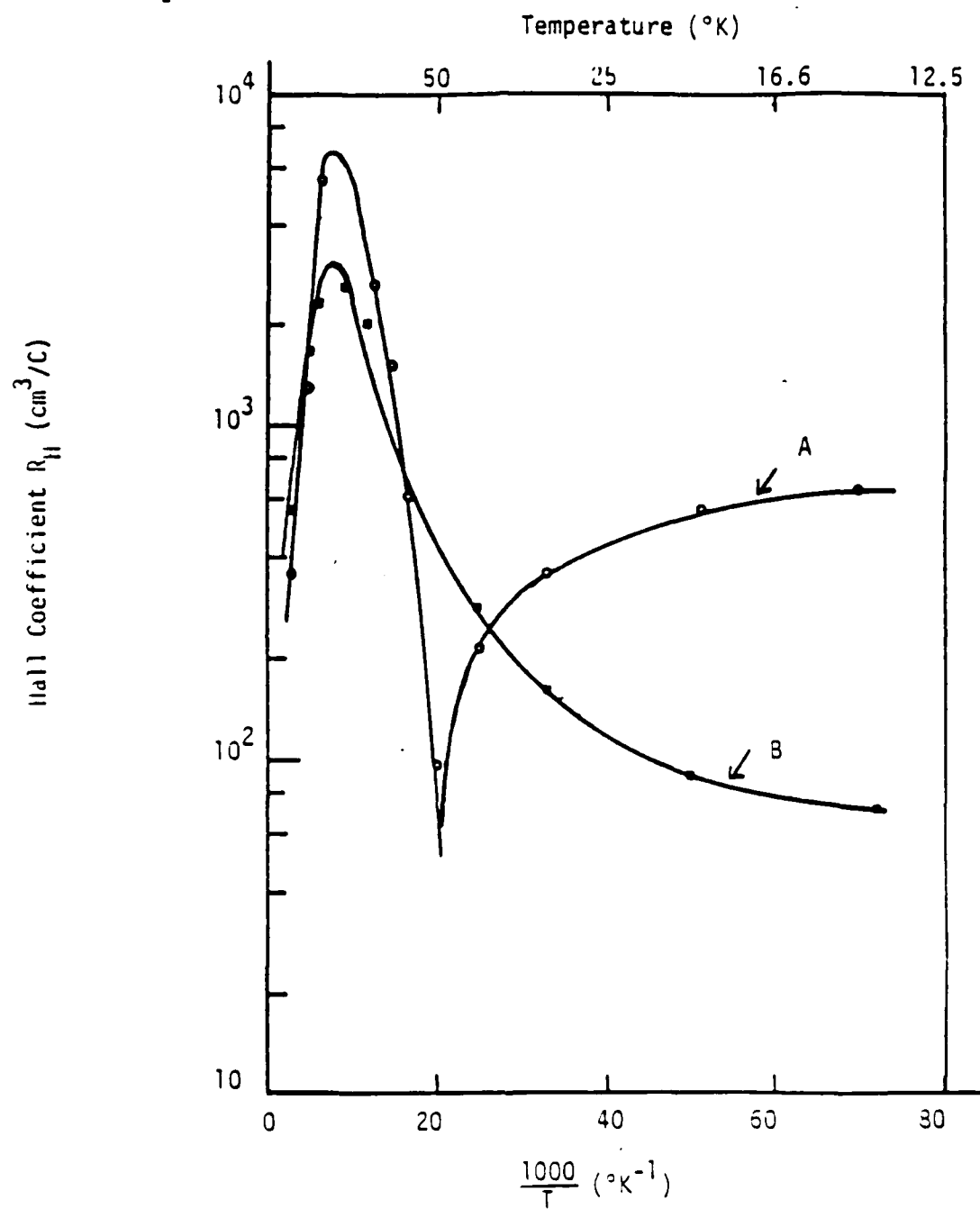
FIG. 7

ON THE MECHANISM OF GROWTH OF CdTe BY ORGANOMETALLIC VAPOR PHASE EPITAXY

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ABSTRACT

This paper presents some experimental results to explain mechanisms involved in the growth of CdTe by organometallic vapor phase epitaxy (OMVPE). A pyrolysis study of dimethylcadmium (DMCd) was conducted in an OMVPE reactor, in the temperature range 230 to 400°C. It was found that dimethylcadmium decomposes above approximately 230°C and the reaction is heterogeneous from 230 to 375°C. CdTe growth was also studied over a range of temperature from 300 to 375°C and for various reactor parameters. In all cases, the CdTe deposition rate was found to be closely related to the decomposition of dimethylcadmium. A model is presented to explain the CdTe growth at low temperatures where diethyltelluride is very stable of itself. CdTe growth, using diethyltelluride and elemental cadmium, was demonstrated, and supports this model. The growth rate of CdTe was studied as a function of the partial pressure of DMCd and DETe, and the results explained in light of this growth model.

1. INTRODUCTION

There is considerable interest (1-6) in the growth of CdTe films, by organometallic vapor phase epitaxy (OMVPE), on a variety of substrates. Recently, the growth of high quality material has been reported by this process. This study is an attempt to increase our understanding of the reaction mechanisms involved during the epitaxial growth of this semiconductor. The study is restricted to the growth of CdTe by the pyrolysis of dimethylcadmium (DMCd) and diethyltelluride (DETe), a commonly used approach for the OMVPE of CdTe today.

The pyrolysis of DMCd has been studied previously in a static system by Laurie and Long (7), at temperatures below 300°C. They proposed that the removal of the first methyl radical is the rate determining step, the second methyl radical detaching itself immediately after removal of the first. From experiments with various surface to volume ratios, it was concluded that the pyrolysis is partly heterogeneous and partly homogeneous. The energy required for the removal of the first methyl radical was found to be 43.5 ± 1.2 Kcal/mole, whereas that for the removal of the second methyl radical was calculated to be 21.4 ± 4 Kcal/mole. Similar studies were conducted by Price and Trotman-Dickerson (8) in a flowing system with toluene as the carrier gas in the temperature range 469-571°C. They also found similar values for the energy required for the removal of the first and second methyl group from DMCd molecule. In addition, they found that the decomposition was homogeneous over this range of temperatures. Although these studies represent a good starting point, the information is of limited value here because of the presence of the other reactants and also because of the presence of large amounts of hydrogen during the OMVPE of CdTe.

A more relevant study of the pyrolysis of DMCd and DETe using
hydrogen as the carrier gas has been reported by Mullin et al., (2). They
carried out the pyrolysis by diluting the alkyl vapors in hydrogen before
feeding them into a heated silica tube. Their study showed that DMCd is
relatively unstable and its decomposition takes place above about $300°C$. On
the other hand, little or no decomposition of DETe was observed below $380°C$.

Quite different results were obtained when DMCd and DETe were
simultaneously introduced into the system. Now, a much higher percentage of
decomposition was observed for the DETe. Also, an appreciable growth rate
of CdTe was observed, even at $350°C$ where DETe was found to be very stable
(2). They have proposed that DMCd and DETe may react to form adducts or
complexes which can decompose at these lower temperatures, to lead to the
formation of CdTe (9).

In a recent paper, Mullin et al., (10) had cast some doubt whether
adduct formation actually takes place in DMCd/DETe systems. Their
observation was based on the work of Czerniak and Easton (11) who conducted
a study of the pyrolysis of DMCd and DETe by in-situ gas sampling and
analysis using a quadrupole mass spectrometer. Their study showed that the
thermal decomposition of DMCd alone occurred in the range $200 - 300°C$
whereas DETe decomposed only above $410°C$. The percentage decomposition
versus temperature curve of DETe was shifted down by $100°C$ in the presence
of DMCd. In addition, the onset of decomposition of DETe fell by about $50°C$
in the presence of Te deposits, suggesting that the DETe decomposition is
auto-catalyzed. No change in the decomposition behavior of DETe was
observed if the reactor tube was previously coated with Cd. Finally, they
found no evidence of adducts (or their fractions) in the reaction chamber.

Kuznetsov, et al., (12) studied the growth of CdTe using $(CH_3)_2Cd$ and $(CH_3)_2Te$ in a hot wall reactor. Growth of CdTe was found to occur in the range 200 - 400 C, where $(CH_3)_2Te$ does not decompose by itself (13). They proposed that $(CH_3)_2Cd$ decomposes into $Cd(CH_3)$ which reacts with $(CH_3)_2Te$, probably forming unstable complexes of the type $[(CH_3)Cd . Te(CH_3)]$, which decomposes with the formation of CdTe. However, no experimental studies were done to establish that complex formation indeed took place.

In this paper, we propose an alternate model to explain the CdTe growth process. Experimental results are presented which support our model, and should be useful in better understanding the actual reaction mechanism involved in the growth process.

2. EXPERIMENTAL

The experimental system used for this study is a conventional OMVPE reactor, of the type used for the growth of HgCdTe, which has been described previously (14). The reaction chamber of this system consists of a 51 mm I.D. horizontal quartz tube, with 10 cm long clam-shell heater in front of an r.f. heated susceptor. The radial uniformity of the clam-shell heater was measured to be $\pm 2^{\circ}C$. Palladium purified hydrogen was used as the carrier gas, and dimethylcadmium and diethyltelluride as the organometallic source chemicals. Single crystal sapphire substrates were used for this study. These were of large area (2 cm^2) to minimize experimental error in the growth data, which was based on weight measurements.

3. RESULTS AND DISCUSSION

(i) Decomposition of DMCd: A decomposition study was carried out by introducing DMCd vapor diluted in hydrogen into the reactor. A series of experiments were conducted with reactor wall temperatures ranging from 230 - 400°C. The total flow was kept at 500 ml/min and the partial pressure of DMCd was kept at 2×10^{-3} atms for all these experiments. The susceptor was not heated for these experiments. However, its temperature was monitored, and found to be under 150°C for all the runs. A large area sapphire substrate was placed on this susceptor and the amount of deposit was measured for each experiment. The material deposited was a conducting film of cadmium, as verified by Energy Dispersive X-Ray Spectroscopy (EDXS).

Figure 1 shows the amount of Cd deposited as a function of reactor wall temperature over the 275-400°C range. It can be assumed here that this amount is a constant fraction of the total amount of DMCd decomposed, since careful attention was placed to susceptor design in order to minimize back-flow in the reactor. A discontinuous film was obtained at reactor wall temperatures below 275°C, so that weight measurement could not be interpreted with accuracyµ hence these data are not shown. However, it should be noted that the discontinuous film was also of cadmium, and growth was observed even at temperatures as low as 230°C.

We note from Fig. 1 that the deposition of Cd was higher than expected at the wall temperature of 400°C. This may be caused by turbulence, which could result in the onset of homogeneous decomposition, in addition to heterogeneous decomposition. We also note the formation of small amounts of black deposits at 400°C. These did not dissolve in concentrated HCl as does cadmium. It is highly probable that DMCd may

polymerize at this temperature to give rise to these deposits (8). However, their exact nature is unclear at the present time.

A decomposition study of DMCd was also made with the reactor wall kept at room temperature, and the susceptor temperature varied from 230 - 360°C. The partial pressure of DMCd was kept in the 2-20 x 10^{-3} atm. range for these experiments. In all cases, no deposit was observed on sapphire substrates placed on the susceptor, although cadmium deposition was observed on the reactor wall in the cooler regions downstream in every case.

Based on this study, we conclude that the decomposition of DMCd is heterogenously catalysed in the temperature range studied. No gas phase Cd formation is expected, at least below 350°C. This conclusion is based on the following observations:

(i)   The activation energy for the deposition of Cd from DMCd was found to be 20.8 Kcal/mole from Fig. 1. This is much lower than the dissociation energy of 45 Kcal/mole reported (8) for the removal of the first methyl-carbon bond. If homogeneous decomposition were dominant, the activation energy of the decomposition would correspond to the breakage of the first methyl bond (7,8) since the second methyl bond is known to detach itself immediately after the removal of the first.

(ii)   When DMCd vapors were passed over the heated substrate, no deposition of Cd was observed even at temperatures as high as 360° C. The partial pressure of DMCd used was many times higher (e.g.,~50 times at 350° C) than the equilibrium vapor pressure of cadmium over cadmium at all growth temperatures.

If the reaction were homogeneous and an appreciable percent of DMCd were to dissociate (11), we would expect Cd deposition on the heated substrate. However, Cd deposition was only observed on the colder regions of the reactor tube downstream.

The activation energy of 20.8 Kcal/mole observed for Cd deposition closely agrees with the dissociation energy (21 Kcal/mole) of the second methyl-carbon bond. From this observation, we conclude that demethylation of the second methyl group is the rate determining step and hence this bond energy may correspond to the activation energy for the DMCd decomposition. This assumes that the removal of the first methyl group is very fast, in this surface catalyzed reaction, even though the dissociation energy for this bond was found to be 45 Kcal/mole in the earlier studies. In addition, the presence of large amounts of hydrogen can also facilitate the removal of the first methyl radical. Alternatively, the equivalence of these two activation energies may be just a coincidence.

We believe that the first hypothesis is more likely here. However, this decomposition study should be repeated on different surfaces or under different reactor flow conditions in order to establish this hypothesis.

(ii) Effect of Temperature on CdTe Deposition: CdTe was deposited on sapphire substrates by introducing DETe vapors into the reactor, in addition to DMCd. The partial pressures of DMCd and DETe both were kept at 2×10^{-3} atms, and the total flow at 500 m ℓ/min. For these experiments, the reactor wall was always kept at room temperature.

Figure 2 shows the variation of the amount of CdTe deposit as a function of substrate temperature. Here, the activation energy for the deposition of CdTe was found to be of about 22 Kcal/mole over the

temperature range investigated. This value agrees reasonably closely with the activation energy measured for the deposition of Cd, in the experiments outlined earlier. This would imply that the amount of CdTe deposited is determined by the amount of DMCd decomposed (if DMCd is not very much in excess). It is also seen that appreciable amount of CdTe deposition was observed, even at 300°C. This agrees very well with the findings of Mullin et al.

The above experiments were repeated for various growth conditions, and the results presented Fig. 3. In all cases, the activation energy for the deposition of CdTe at low temperatures (< 350°C) was found to be~22 Kcal/mole, within experimental error. However, lowering the total flow rate or the reactant partial pressure had a pronounced effect on the growth behavior at higher temperatures. For example, a fall off in the deposition rate is observed above 400°C when the total gas flow was 1 ℓ/min in Figure 3. This is because of the increased reactant depletion on the reactor wall in front of the susceptor. Increasing the gas velocity in the system, while keeping reactant pressures constant, resulted in eliminating this fall off, and supports this observation.
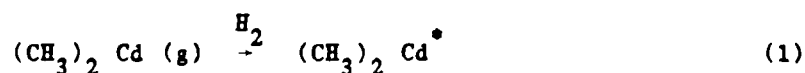
The values reported in the literature for the activation energy of CdTe deposition are not in complete agreement. Mullin, et al., (2) have used (100) single crystal CdTe and observed a constant growth rate from 500°C down to about 360°C, and then a sharp fall off at lower temperatures, with an activation energy of 75 Kcal/mole. They have suggested that the high value observed here is caused by the difficulty of nucleating on a single crystal substrate. Cole et al (15) have also observed a similar sharp fall off in the growth rate with a decrease in temperature, even though they used sapphire substrates. Ghandhi and Bhat (4) have observed a
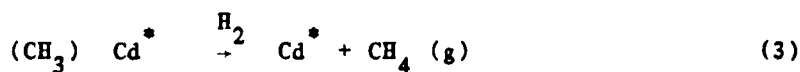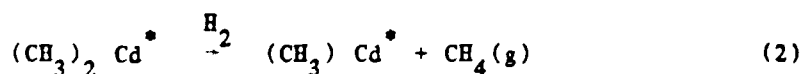
value of 16 Kcal/mole when the growth was done on InSb substrates over the 350-400 °C temperature range. However, in all the above studies, the number of experimental points below 360°C are too few to make any definitive judgment.

Kuznetsov, et al., (12) have observed an activation energy of approximately 24 Kcal/mole for CdTe deposition on (0001)S CdS substrates using $(CH_3)_2Cd$ and $(CH_3)_2Te$ in H_2. They observed the same value when CdSe was grown on (111)GaP using $(CH_3)_2Cd$ and $(CH_3)_2Se$ (16). In this work, which was carried out over the 250 - 480°C range, we have consistently observed a value of around 22 Kcal/mole for temperatures below 350°C.

(iii) CdTe Growth Using DETe and Elemental Cd: CdTe growth was carried out by introducing elemental Cd vapor into the reactor, with DETe as the Te source. The growth was done with the reactor wall and the susceptor both kept at the same temperature. A total flow of 500 mℓ/min was used. The growth of CdTe was accomplished on both sapphire and cadmium telluride substrates at temperatures as low as 230°C, where DETe is very stable of itself. Infrared transmission measurements have shown that the deposits were indeed single crystal CdTe. It is seen from this result that the presence of elemental Cd enhances the decomposition of DETe. Moreover, we have shown earlier that the presence of DMCd also enhances the decomposition of DETe.

(iv). Growth Model: Based on the preceeding experiments, we propose that the CdTe deposition occurs by the following mechanisms:

$$(CH_3)_2 \ Cd \ (g) \ \xrightarrow{H_2} \ (CH_3)_2 \ Cd^* \qquad\qquad (1)$$

$$(CH_3)_2 \; Cd^* \quad \xrightarrow{H_2} \quad (CH_3) \; Cd^* + CH_4(g) \tag{2}$$

$$(CH_3) \; Cd^* \quad \xrightarrow{H_2} \quad Cd^* + CH_4 \; (g) \tag{3}$$

where * represents adsorbed molecules.

If reaction (2) is fast compared to reaction (3), (which is possible, because of its heterogenous nature) the activation energy for the Cd deposition would correspond to the dissociation energy of the second methyl-carbon bond.

In the absence of any DETe, the decomposed Cd may leave the surface, because no overpressure of Cd is present to prevent its evaporation in a flowing open tube system. If DETe is present however, it can be physisorbed, accompanied by surface diffusion. Now, the decomposition DETe can be enhanced by the presence of Cd^*, as follows:

$$Cd^* + (C_2H_5)_2 \; Te^* \quad \xrightarrow{H_2} \quad 2C_2H_6 \; + CdTe(s) \tag{4}$$
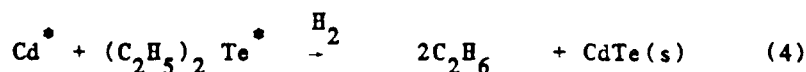
The above reaction is probable because the establishment of the Cd-Te bond can facilitate the breaking of the Te-ethyl bond of DETe molecules adsorbed on or near cadmium. The vapor pressure of both of the elements over CdTe is low, [less than 10^{-8} torr at 350°C over CdTe (17)], so that evaporation of CdTe is not expected. However, the growth rate will be

limited by the kinetic processes which determine the decomposition of DMCd and physisorption and surface diffusion of DETe. In the present case, reaction (3) will be the rate determining step below 350°C.

The process described here, i.e., the heterogeneous decomposition of organometallics, has been observed in other systems as well. For example, trimethylgallium breaks down (18) on arsenic coated surfaces at temperatures in the vicinity of 285°C. In contrast, the decomposition of trimethylgallium into gallium in the absence of As bearing species only occurs at temperatures above 800°C. This observation also renders support to the above argument. The same type of behavior was observed by Kuznetsov, et al. (13), in the growth of CdTe and CdSe. In their study of the growth of CdTe using $(CH_3)_2Cd$ and $(CH_3)_2Te$, it was reported that the activation energy for the growth was 25 Kcal/mole in the 200 – 300 °C range. The same value was also observed by these authors (16) in case of CdSe deposition, using $(CH_3)_2Cd$ and $(CH_3)_2Se$. Both studies suggest that the decomposition of the second methyl group from the dimethylcadmium is the rate limiting step in the growth.

In a mass spectrometric study of DETe decomposition, Czerniak and Easton (11) did not observe any difference whether the reactor wall were pre-coated with Cd or not. This does not contradict our observation here because a pre-coated reactor will become covered with a monolayer of CdTe, once the DETe is introduced. In our case, there is a steady supply of Cd so that a fresh Cd surface is continually generated. Moreover, using an elemental Cd source, we have shown in this work that CdTe can be grown at temperatures as low as 230°C, where DETe is found to be very stable.

(iv) CdTe Growth from DMCd and DETe: We have grown CdTe on Al_2O_3, (100) CdTe, (100) GaAs and (100) InSb substrates, using DMCd and DETe as the alkyl sources. Essentially, similar growth characteristics were noted, and are illustrated here for the case of CdTe on InSb. Figure 4 shows the effect of increasing the DETe flow rate on the growth rate of CdTe. For these experiments, the partial pressure of DMCd (P_{DMCd}) was kept at 1×10^{-4} atm. with a total flow of 3ℓ /min. The susceptor temperature was 360°C. The growth rate is sublinear with P_{DETe} and finally saturates for a P_{DMCd}/P_{DETe} ratio of approximately 6. One important observation is that the growth rate of CdTe continues to increase even when $P_{DETe} > P_{DMCd}$.

On the other hand, the effect of DMCd on the growth rate (see Fig. 5) is different to that of Fig. 4. Here, growth rate curves are shown for two different values of P_{DETe}. It is seen that the CdTe growth rate saturates for $P_{DMCd} > P_{DETe}$.

The following conclusions can be drawn from these data. First, the growth rate is sublinear with both P_{DMCd} and P_{DETe} and can be modelled using a Langmuir-Hinshelwood mechanism (14,19). This suggests that the growth is kinetically controlled, even at 360°C. However, the rate limiting step in the growth at this temperature is not the decomposition of DMCd, because complete decomposition to Cd is expected to occur (2,12). Next, the difference in the growth behavior with P_{DMCd} and P_{DETe} suggests that the adsorption to desorption rate of DMCd is very high compared to that of DETe. This comes about because DMCd decomposes into Cd and becomes chemisorbed soon after adsorption. On the other hand no such reaction occurs in case of DETe, until DETe come in the vicinity of the adsorbed Cd molecules.

These observations also support the arguments of the proposed growth model.

CONCLUSION

The pyrolysis of DMCd in hydrogen was studied in order to obtain information about the reaction mechanisms involved in CdTe growth. It was found that DMCd decomposed above approximately 230°C and that the reaction was heterogeneous. CdTe growth was also studied over a range of temperatures from 300°C - 375°C. Here, the CdTe deposition rate was closely related to the decomposition rate of DMCd. A model was presented to explain CdTe growth at low temperatures, where DETe is known to be stable. CdTe growth was also carried out at 250°C using DETe and elemental Cd to support this model. The growth rate of CdTe was also studied as a function of P_{DETe} and P_{DMCd}, again the result support the above growth model.

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FIGURES

Figure 1   Amount of Cd deposit in 30 min. as a function of reactor wall
             temperature.

Figure 2   Amount of CdTe deposit in 30 min. as a function of susceptor
             temperature, T.

Figure 3   Amount of CdTe deposit in 30 min. as a function of susceptor
             temperature, for various reactor conditions:

             $\square$, $P_{DETe} = 3 \times 10^{-4}$ atm, $P_{DMCd} = 1 \times 10^{-4}$ atm, total flow =
             1 ℓ/min.

             $\bigcirc$, Same as above, but total flow = 3 ℓ/min.

             $\triangle$, $P_{DMCd} = 3 \times 10^{-4}$ atm, $P_{DETe} = 1 \times 10^{-4}$ atm, total flow =
             1 ℓ/min.

Figure 4   Growth rate of CdTe on InSb at 360° C, as a function of P_{DETe}.

             $P_{DMCd} = 1 \times 10^{-4}$ atmµ total flow = 3 ℓ/min.

Figure 5   Growth rate of CdTe on InSb at 360° C, as a function of P_{DMCd}.

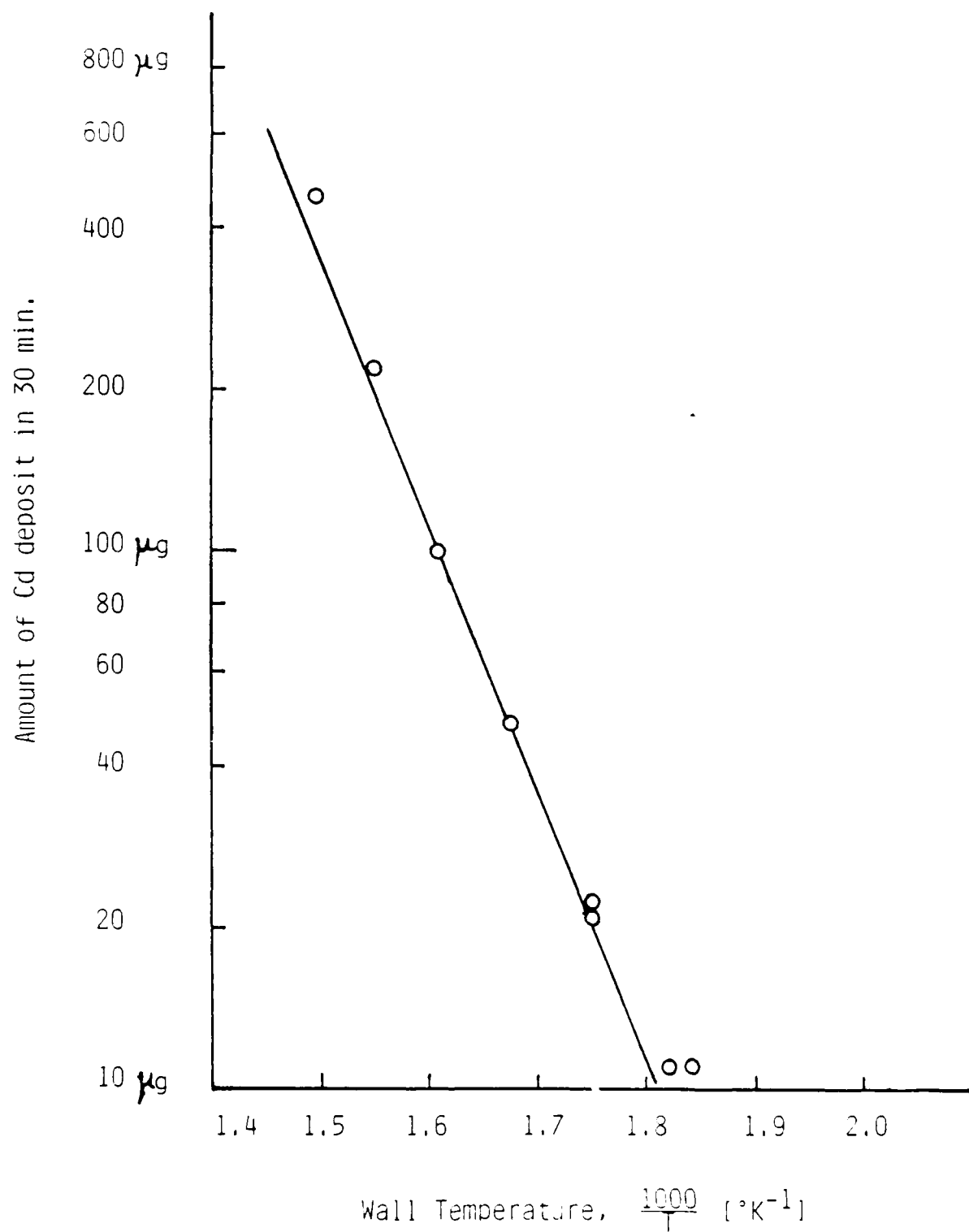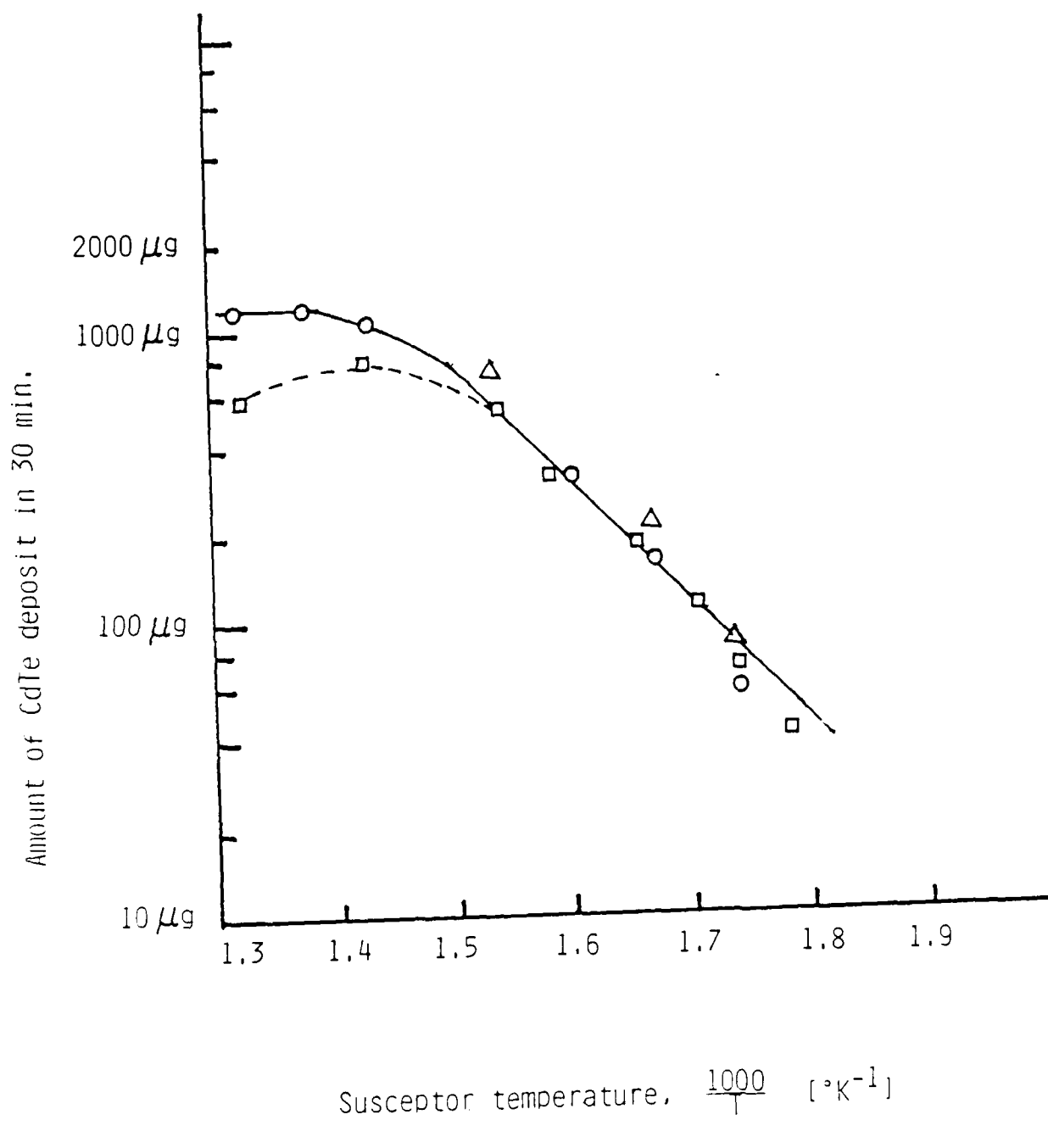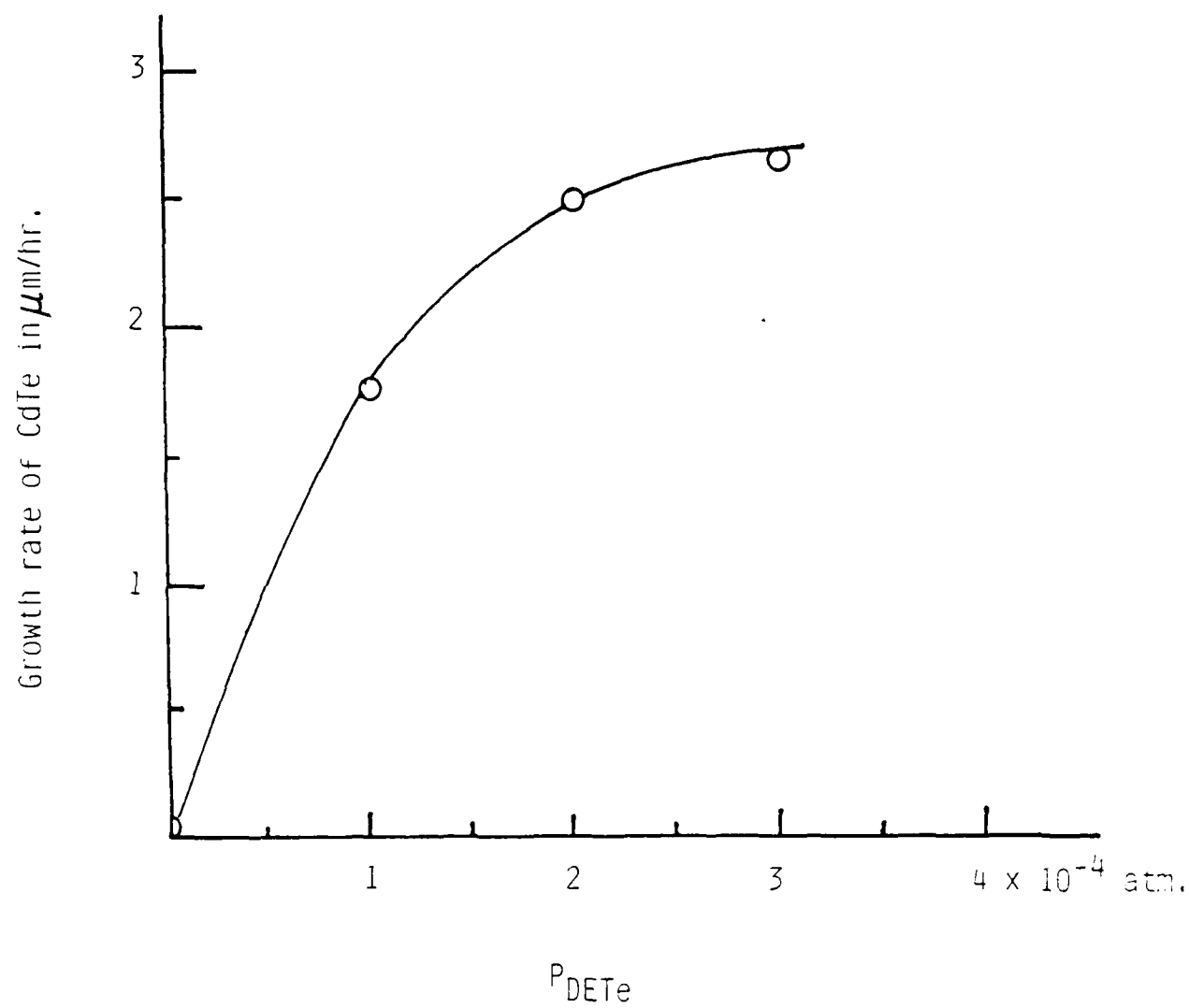   Total flow = 3 ℓ/min.

FIG.1

FIG.2

Amount of CdTe deposit in 30 min.

Susceptor temperature, $\dfrac{1000}{T}$ $[°K^{-1}]$

FIG.3

FIG 4

FIG.5

END

DTIC

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